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# Transactions of the Faraday Society.
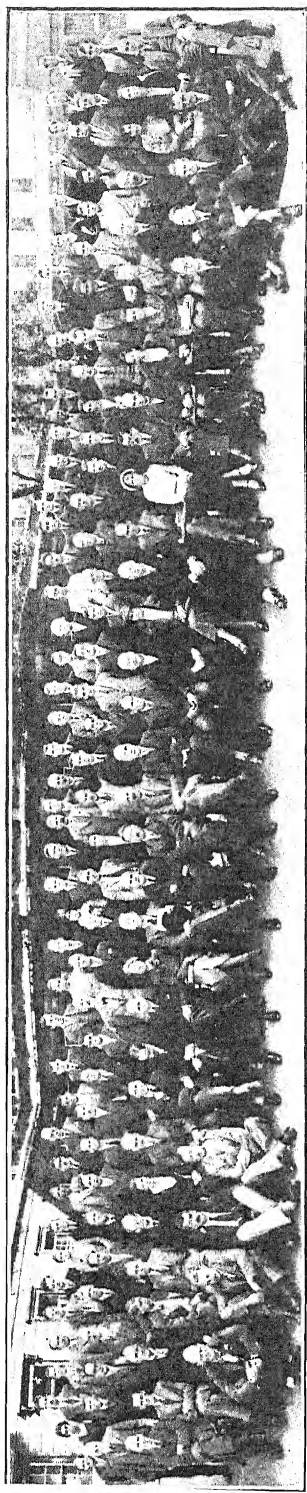
# VOL. XXXI. 1935

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# THE FARADAY SOCIETY.

## GENERAL DISCUSSION ON COLLOIDAL ELECTROLYTES.

### University College, London, 27th to 29th September, 1934.

The above is a reproduction on a reduced scale of a photograph of those attending the meeting on 28th September.

Seated in the front row, reading from left to right are:—Dr. G. F. Davidson, Dr. C. Robinson, Prof. W. C. M. Lewis, Dr. O. Quensel, Mr. Macfarlane, Dr. G. S. Adair. Mme. A. Roche, Prof. E. Gorter, Prof. E. K. Rideal, Prof. A. Frumkin, Prof. E. Elöd, Miss D. Jordan-Lloyd. Dr. F. A. Freeth. Mr. W. Rintoul. Prof. H. Freundlich, Prof. H. R. Kruyt, Prof. F. G. Donnan, Dr. F. Eirich Prof. I. Traube, Mrs. Laing-McBain. Prof. Wo. Ostwald. Prof. E. J. Bigwood, Fraulein Krüger, Prof. A. J. Rabinovitch, Dr. Ph. Gross, Mrs. J. W. Goodeve, Fraulein G. Kornfeld. Dr. E. Valkö. Prof. W. D. Treadwell, Mr. E. Hatschek, Fraulein L. Werner, Miss G. Wakeley and Prof. C. K. Ingold.

*Copies of the full-scale photograph (four times this size) may be obtained from the photographers: Messrs. London Panoramic Co., 10 Farringdon Avenue, London, E.C. 4, to whom application should be made.*

# A GENERAL DISCUSSION ON COLLOIDAL ELECTROLYTES.

*Thursday, 27th September to Saturday, 29th September, 1934.*

THE SIXTY-FIRST GENERAL DISCUSSION of the FARADAY SOCIETY (being the Third Colloid Meeting organised by the Colloid Committee of the Faraday Society, which comprises representatives of the Royal Society, the Biochemical Society, the Chemical Society, the Faraday Society, the Physical Society, the Physiological Society and the Society of Chemical Industry) was held at University College, University of London, from the 27th to the 29th September, 1934, inclusive.

The subject was discussed approximately under the following heads :

## PART I.—GENERAL.
(*a*) Theory.
(*b*) Methods and Experimental Technique.

## PART II.—SPECIAL AND TECHNICAL.
(*a*) Soaps and other Long-Chain Colloidal Electrolytes.
(*b*) Dyestuffs.
(*c*) Silicates and Silicic Acid.
(*d*) Proteins.
(*e*) Other Substances.

The meeting was held in the Chemistry Theatre at University College. Professor F. G. Donnan, F.R.S. (a Past-President of the Faraday Society) occupied the Chair. By the courtesy of the Provost and the Refectory Committee, the Guest Night Dinner was held on Thursday evening, 27th September, in the Refectory in honour of the overseas guests of the Society. There were no formal speeches, but the toast of the overseas guests was proposed by the Chairman and a reply was given by Professor Ostwald. The toast of University College was proposed by Professor Kruyt and the Provost of University College replied. Those attending the meeting found it a great convenience that arrangements were made for all meals to be taken in the Refectory during the period of the meeting. On Friday evening the overseas guests were given private hospitality.

At the Inaugural Meeting, the Chairman introduced the overseas members and visitors and guests of the Society and called upon them each to rise in his place so that they might be welcomed with acclamation by the Society. Those so welcomed were : Professor E. J. Bigwood

(*Brussels*), Dr. Eva Ehrlich, (*Utrecht*), Dr. F. Eirich (*Wien*), Professor E. Elöd (*Karlsruhe*), Professor A. Frumkin (*Moscow*), Professor E. Gorter (*Leiden*), Dr. P. Gross (*Wien*), Professor and Mrs. Hammarsten (*Stockholm*), Professor H. R. Kruyt (*Utrecht*), Fräulein Dr. Kruger (*Berlin*), Mrs. J. W. McBain (*Stanford*), Dr. M. Meyer (*Leiden*), Dr. J. L. van der Minne (*Amsterdam*), Dr. H. Neurath (*Wien*), Mr. J. van Ormondt (*Leiden*), Professor Wo. Ostwald (*Leipzig*), Dr. O. Quensel (*Upsala*), Professor A. J. Rabinovitch (*Moscow*), Madame A. Roche (*Marseilles*), Professor W. D. Treadwell (*Zürich*), Dr. E. Valkó (*Ludwigshafen a/Rh*), and Professor F. Weigert (*Leipzig*).    In addition the Chairman took the opportunity of welcoming to the meeting a number of overseas members and visitors at present resident in Great Britain, and in particular mentioned Professor H. Freundlich, Professor F. Simon, Dr. Gertrud Kornfeld and Professor I. Traube.

The Secretary read letters from the following guests who had un-avoidably been prevented from being present : Professor P. Debye, Dr. K. Linderstrøm-Lang, Professor A. Lottermoser, Professor J. W. McBain, Professor W. Pauli, Professor M. Samec. The Chairman also conveyed to the meeting the apologies and good wishes of the President, Dr. N. V. Sidgwick, who had not been able to return from a visit to America in time to attend the meeting.

The general Introductory Statement was then given by Professor H. Freundlich, after which the various papers, which had been cir-culated in advance, were discussed.   The papers and the discussion thereon appear in the following pages.

At the commencement of the second session of this, the third and last Colloid Meeting which the Faraday Society had definitely agreed to hold, Professor Rideal and Professor Donnan paid tribute to the memory of the founder of the Colloid Committee and of these meetings, the late Sir William B. Hardy.

Professor E. K. Rideal said : Ladies and Gentlemen, I would like to draw your attention to the fact that this is the first meeting of the Faraday Society, arranged by the Colloid Committee of that Society, to be held after the death of the founder of these meetings, Sir William Hardy.   Some of you may have known him, many of you must have read of his work and all of you must have heard of him.   I feel sure that nothing would have pleased him more than to view the attendance at this meeting and to receive an assurance that future meetings would be held in the same spirit and with the same objects in view as has animated the Committee which Sir William originally founded.   It has occurred to me that we could show no better sign of our appreciation of his personality and work than to arrange for the publication of his collected papers.   If this is thought desirable I would be willing to explore this avenue and approach Lady Hardy on the matter.

Professor F. G. Donnan said: It gives me great pleasure to endorse very heartily everything Professor Rideal has said about the late Sir William B. Hardy.   The initiation of the General Discussions of this Society on Colloid Science and the formation of the Colloid Committee are due to him.   I shall regard it as a privilege to be allowed to lend active support to any plan for the commemoration of the great scientific work which he did, and I am sure that this Society and many others will take the same view.

These speeches were received with great sympathy.

The Meeting received with keen appreciation a suggestion that the Council of the Faraday Society should be invited to continue the work of the Colloid Committee, in collaboration with all the other societies represented on that Committee, by holding further meetings, preferably at times which did not clash with the biennial meetings of the Kolloid Gesellschaft.

At the conclusion of the meeting a vote of thanks was accorded at the instance of the Chairman to the overseas guests for their presence and assistance in the success of the meeting, and Professor Kruyt replied. On the motion of Professor Rideal, votes of thanks were accorded to the Provost, to the Chairman, to Mr. Goodeve and his colleagues at University College, to Mr. Kettel and the laboratory staff, and to the Superintendent and staff of the Refectory, and also to Mr. Marlow, the Secretary, and Miss Wakeley. Professor Donnan replied. Professor Donnan then proposed a vote of thanks to the contributors of papers and contributors to the discussion, and to the organising committee, naming particularly Professor Freundlich. He also proposed a special vote of thanks to the lady guests and contributors. These were all received with acclamation.

In conclusion, Professor Donnan expressed the appreciation of all at the presence of Professor Ostwald with them. Professor Ostwald had scarcely recovered from his labours in organising the successful meeting of the Kolloid Gesellschaft, and they hoped that in future years it would be possible to avoid holding these two important meetings in the same year. Professor Ostwald, in reply, agreed that colloid chemists worked hard but they enjoyed it.

# GENERAL INTRODUCTION.

## COLLOIDAL ELECTROLYTES; THEIR NATURE AND IMPORTANCE FOR COLLOIDAL SCIENCE.

By H. Freundlich (*University College, London*).

*Received, 29th August, 1934.*

Classifications are necessary, but are frequently open to objection. This is specially so in the domain of colloids, and it is often a matter of doubt, whether a given colloid belongs to one class or another. Discussions of this kind are rarely fertile and this makes the whole question of classification in my opinion rather uninteresting.

Now, the class of colloids, which we are going to discuss in this meeting, the colloidal electrolytes, have attracted more and more interest during the last ten or twenty years. The term " colloidal electrolyte " does not give us the clue for this popularity. It is, taken literally, a very general term, expressing merely the fact that we have colloidal systems, which show (in regard to dialysis, Tyndall-phenomenon, etc.), the properties characteristic for these systems, but which also manifest a well-defined electrical conductivity of a type characteristic of electrolytes, that is to say, caused by ions ; these ions have in the case of colloids a very high valency. In this general sense the notion of a " colloidal electrolyte " was first used by Duclaux,[1] and it is also applied in this way nowadays by a number of investigators (Pauli).[2]

Mcbain,[3] however, very soon used the term in a more specialised way, for a special kind of substance, and thus changed its significance in a certain sense which made it so valuable as a principle of classification. He investigated the alkali salts of the fatty acids as electrolytes, their conductivity, hydrolysis, etc., ascending in the homologous series. The lower members, such as potassium acetate or propionate are undoubtedly strong electrolytes in true solution, like so many other salts of organic acids. But the higher members such as potassium palmitate or stearate show distinct anomalies as electrolytes, owing to the fact that a certain percentage of the dissolved substance has colloidal properties. We have not only to deal with alkali cations and the anions of the fatty acid, but with larger particles mostly of colloidal dimensions, and particularly with large anions built up of a large number of the monomeric anions of the fatty acid, but containing also alkali metal, water, etc. These " micelles " or " micellar ions " are the cause of the anomalous behaviour of the soaps as electrolytes. Now, these salts of the higher fatty acids can be prepared with practically the same degree of purity as those of the lower acids, if we neutralise for instance the organic acid dissolved in an organic liquid ; in these both the fatty acid and the soap are in true solution.

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[1] Duclaux, *J. chim. physique*, **7**, 405, 1909; compare also Malfitano, *C.R.*, **148**, 1045, 1909.
[2] Pauli and Valkó, *Elektrochemie der Kolloide*, 1929.
[3] Compare McBain and collaborators, *J. Chem. Soc.*, **101**, 2042, 1912 ; **105**, 417, 957, 1914 ; **113**, 825, 1918.

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We have, thus, the possibility of preparing " pure " substances, in the regular sense of the word, but these substances manifest a colloidal behaviour, when dissolved in a suitable solvent, such as water. This property is not expressed in the term " colloidal electrolyte," but taken for granted, since soaps were for a long time the main type of colloidal electrolyte ; and this is the property which many investigators consider a valuable principle of classification, and I agree absolutely with this opinion. For very many other colloidal systems contain substances which are not pure in the common sense of the word and which cannot be purified with certainty, such as the sols of metals, oxides, etc. A colloidal solution of gold, for instance, contains particles of gold : the X-ray spectrum proves this beyond doubt ; the electrical properties of the sol are caused by a small amount of a foreign electrolyte, the " active electrolyte," bound to the gold-particles by adsorption or by some loose chemical union. The colloidal electrolytes on the other hand are char-/ acterised by the fact that they form ions of colloidal size spontaneously ; the electrical charge is bound to a high percentage of the dissolved substance itself, not to that small amount of active electrolyte which may be separated more or less easily from the bulk of the colloidal particles, as in the case of colloidal gold or sulphur. Owing to this we may prepare stable colloidal solutions having well-defined, reproducible electrical properties easily.

Now the number of known colloidal electrolytes (as a special class of colloids) have grown strongly and steadily in number. On the one hand we have been able to prepare all sorts of new groups of pure substances showing colloidal properties, when dissolved in water; on the other hand it has been possible to prove that well-known substances in solution behaved like pure colloidal substances, manifesting for instance a well-defined molecular weight. Simultaneously with McBain's investigation of soaps, Reychler [4] showed that cetyl sulphonic acid and its salts behave very similarly to soaps. This was the first member of a new and most important class of colloidal electrolytes ; it is known that in the course of recent years a great number of sulphonic acids of long-chain compounds have been prepared and that they and their salts have turned out to be technically valuable as detergents, as foam-producers, etc. As an alkaline counterpart to this acid group, long-chain amino-compounds were prepared. [5] It is obvious that many dyestuffs, for instance those of the congo-group, belong to this class ; some of them have been prepared already in a pure form, [6] but apart from this, their behaviour is so similar to that of the salts of sulphonic acids or of long-chain amines that their relationship is not to be doubted. When Svedberg developed the ultracentrifuge and showed that many proteins had large, but well-defined molecular weights, it was most probable that proteins were chemical entities, at least in a certain range of $p_H$. Since proteins are electrolytes too, one is justified in adding them to the class of colloidal electrolytes. In very many other cases, for instance in the case of silicates, of salvarsans, of some compounds of starch, etc., opinions may differ still, how far they belong to this group or not, but it is not unlikely that many do. Many may belong to a very general class of colloidal

[4] Reychler, *Kolloid-Z.*, **12**, 278, 1913 ; **13**, 252, 1913.
[5] Krafft (*Ber. deutsch. chem. Gesellsch.*, **29**, 1330, 1896) has remarked already that $C_{16}H_{33}NH_2$ . HCl behaves as a soap-like colloid in aqueous solution.
[6] C. Robinson and H. A. J. Mills, *Proc. Roy. Soc.*, **131A**, 576, 1931.

electrolytes consisting of esters of multivalent acids with alcohols of very high molecular weight.[7]

In the ideal case we may prepare the pure colloidal electrolyte like any other pure chemical compound and then dissolve it in water, for instance. We need not powder it extremely finely or peptise it by adding a special peptising agent; it is not necessary to have a small excess of anion or cation, as is the case if we wish to peptise salts such as the silver halides, for instance. The colloidal electrolyte dissolves as such, and forms the colloidal solution. It has in many cases, therefore, a true solubility. It is certainly quite possible that equilibrium is not established so quickly and smoothly as in true solutions of substances having a low molecular weight. Cases of very obstinate supersaturation are not improbable when dealing with colloidal electrolytes and are found in fact. An example of this kind is the behaviour of uric acid and its salts.[8]

I have mentioned already as a characteristic property of colloidal electrolytes that they form a large amount of ions out of the bulk of the substance. Since we have a certain amount of large colloidal ions in addition to small ions of the opposite sign in stable solution extending over a fairly wide range of concentrations, some classes of colloidal electrolytes are excellently suited for investigating Donnan equilibria and the membrane-potentials caused by them. I shall discuss later the marks of distinction which characterise these special classes of colloidal electrolytes. It is the difference in size which allows us to separate small and large ions and to bring about the phenomena just mentioned. We may always also separate the two kinds of ions to a certain degree by centrifugal forces ; in this way we may produce centrifugal potentials, as Svedberg[9] did when investigating proteins with the ultracentrifuge.

Both in the case of Donnan equilibria and of centrifugal potentials, the presence of other kinds of ions is of great importance and it always makes a special treatment necessary. The same holds for the free diffusion of colloidal electrolytes. We must apply the law governing the diffusion of a salt with a multivalent ion. The velocity of diffusion is strongly influenced by diffusion potentials, caused by the difference in velocity of the two ions, and the value of these potentials again depends upon the total concentration of the ions in the solution.[10]

The ionic micelles are large and are highly charged. As we can pass from true solutions of salts of low fatty acids quite gradually to the colloidal solutions of soaps, why should we not try to apply conceptions to these large and highly charged ions which have proved useful in the case of true solutions of small and not highly charged ions ? In other words, it is worth while to try to apply the Debye-Hückel theory to these solutions of colloidal electrolytes. This has been done in different ways. It is a serious difficulty that two factors—size and charge— are changed, and we are not able to investigate the influence of each separately.

[7] Compare for instance Haas and Hill, *Ann. appl. Biol.*, **7**, 352, 1921 ; *Biochem. J.*, **15**, 469, 1921; Russell-Wells, *ibid.*, **16**, 578, 1922; Harwood, *J. Chem. Soc.*, **123**, 2254, 1923.

[8] Compare H. Freundlich and L. Farmer Loeb, *Biochem. Z.*, **180**, 141, 1926 ; G. Ettisch, L. Farmer Loeb and B. Lange, *Biochem. Z.*, **184**, 257, 1927.

[9] Svedberg, *Zsigmondy-Festschr. Ergänzungsb.*, *Kolloid-Z.*, **36**, 53, 1925 ; Tiselius, *Z. physik. Chem.*, **124**, 449, 1926.

[10] Bruins, *Kolloid-Z.*, **57**, 152, 1931 ; G. S. Hartley and C. Robinson, *Proc. Roy. Soc.*, **134**A, 20, 1931. Compare also McBain and Liu, *J. Am. Chem. Soc.*, **53**, 59, 1931.

As to the nature of these large ions, we seem to have two limiting cases. The one is represented by soap solutions and many similar systems, such as solutions of salts of sulpho-acids and long-chain amino-compounds, dyestuffs, etc. In these the monomeric form of the single ion, for instance the anion of the fatty acid, exists in addition to the micelles, the latter being built up of a large number of simple ions. We may have a reversible equilibrium between these two compounds. On applying the mass-law, as Bury [11] did, we have :

$$m = \kappa s^n$$

where $s$ is the concentration of the simple ion, $m$ that of the ionic micelles, and $\kappa$ and $n$ are constants. It is evident that $m$ increases, when $s$ and, with it, the total concentration, increases, and it may be readily shown that this rise is very steep, if $n$ is large and $\kappa$ small. It is owing to this that Lottermoser [12] found in solutions of salts of long-chain sulpho-acids a strong drop of the equivalent conductivity, as soon as a certain concentration was reached.

Thus we meet the micelles in concentrated solutions. In low concentrations, two possibilities occur. The micelles may dissociate into monomeric ions of so small molecular weight that the solution behaves as a true solution. Its particles dialyse through membranes. A concentrated solution of this kind also does not behave like a normal colloidal solution on dialysis, because a certain percentage of small monomeric ions is always present ; these diffuse through the membrane, the decrease of concentration causes micelles to dissociate and, thus, the dissolved substance passes through the membrane till the concentration is the same on both sides. Solutions of soaps belong to this type.

The other possibility is that the monomeric ions, or, to put it more generally, the ions of lower molecular weight formed out of the micelles on dissociation, do not dialyse. Then the dilute solution will retain colloidal properties to a certain extent. Many dyestuffs, for instance those of the congo-group, belong to this type of colloidal electrolyte. I leave it undecided, whether this behaviour is caused by the size of these ions, or whether their other properties—for instance their adsorption on the membrane or their tendency to form micelles—or properties of the membrane—for instance membrane potentials—are responsible for this behaviour.

A rather surprising difference between the behaviour of micelles and monomeric ions was noticed by McBain [13] : although the ionic micelles are large and we might therefore anticipate a small mobility, they often have a higher mobility than the simple ions, owing to their high electric charge. This specific property of the ionic micelles is, of course, the main cause of the anomalous behaviour of the conductivity in these solutions.

It is an interesting question, discussed by G. S. Hartley, how far the micelles are, so to say, homoionic, consisting of monomeric ions of one kind, or whether they may be polyionic, ions of another kind being perhaps capable of substituting the original ions to a certain degree.

The other limiting case of ionic micelles is most probably found in the solutions of many proteins.[14] In these the micelles are not sensible

[11] Bury and Grindley, *J. Chem. Soc.*, 679, 1929.
[12] Lottermoser and Püschel, *Kolloid-Z.*, **63**, 175, 1933.
[13] McBain, *Kolloid-Z.*, **12**, 256, 1913.
[14] Compare, as to the facts in this paragraph, papers of Svedberg and his collaborators, J. *Amer. Chem. Soc.*, **50**, 3318, 1928 ; **51**, 539, 550, 1929 ; **52**, 2855, 1930.

to dilution, they do not decompose into monomeric ions, but remain unchanged with the same molecular weight in all concentrations, so far as has at present been investigated. This only holds for a certain range of $p_H$, characteristic of every protein. Outside this range the large particles decompose into smaller fragments. In some cases this change is reversible : if the $p_H$ is brought back to the range of stability, the same large particles are formed. Nevertheless, irreversible changes seem to be more frequent. There are a few cases known, too, where large particles of proteins are reversibly changed on dilution, for instance in solutions of serum-albumin and of L-hæmocyanine. The nature of these fragments has not been investigated very thoroughly ; they do not, however, seem to be monomeric ions, as in the first type we discussed, but fairly large particles whose molecular weight is a simple fraction of that of the original protein.

It is important to point out to the following fact. We have met with three possible types of colloidal electrolytes : 1. The ionic micelles are sensible to dilution, forming small monomeric ions which can be dialysed (example : soaps) ; 2. They are sensible to dilution, but form ions as products of dissociation which cannot be dialysed (example : congo-dyestuffs) ; 3. They are practically not sensible to dilution (example : some proteins). Only types 2 and 3 are suitable for investigating the Donnan equilibrium and the membrane-potentials caused by it. Moreover we may expect to find such equilibria in biological and technical systems, as soon as these two types of colloidal electrolytes are separated from other solutions by membranes impermeable to the colloidal ions contained in these solutions.

A special feature of protein solutions is their amphoteric nature. This causes the great differences in behaviour at the isoelectric point or in solutions whose $p_H$ lies on the one or the other side of this point. A high concentration of *zwitterions* is, most likely, decisive for the behaviour at the isoelectric point, and their constitution is to some extent different from that of the ions which are stablein a m ore acid or more alkaline solution. The *zwitterions* are more compact and presumably less hydrated than the loosely built ions found outside the isoelectric point.[15]

Salvarsan and similar compounds also form solution of colloidal electrolytes of an amphoteric nature.[16] It might be worth while to investigate them more exactly, since they have a simpler constitution than the proteins.

I have, so far, not mentioned that, on the whole, the particle size of colloidal electrolytes is not so very great ; the molecular weight ranges as a rule between a few thousands and some 100,000. This holds, at any rate, for that type to which the soaps belong. As to the proteins, most of the better known substances, such as the albumins, hæmoglobin, etc., also have molecular weights in this range. There are certainly some (*e.g.*, the hæmocyanins) with molecular weights going into the millions. But we shall not be very wrong, if we distinguish colloidal electrolytes from other colloids as being a class containing comparatively small particles.

In distinguishing them from true solutions it might be said that most probably very many more solutions of electrolytes contain a small amount

[15] Pauli and Valkó, *Kolloidchemie der Eiweisskörper*, 2nd edition, 1933.
[16] A. S. Hunter and W. A. Patrick, *J. Lab. and Clin. Med.*, **10**, 343, 446, 1925 ; C. Robinson and C. A. Morrell, *Trans. Faraday Soc.*, **30**, 339, 1934.

of ionic micelles and so really belong to this type of colloids, than we imagine. We have not very exact methods for discovering micelles of rather small size. But anomalies in the electrical behaviour, the conductivity, the transport number, etc., are certain to be found in many concentrated solutions of electrolytes and they may be often due to the presence of ionic micelles. In the case of dyestuffs for instance it is not easy to state which of them really gives true solutions. Even a substance diffusing so rapidly as methylene blue shows, according to C. Robinson, anomalies in the conductivity of its aqueous solutions, characteristic of colloidal electrolytes ; picric acid is one of the small number of dyestuffs not showing any anomalies of this kind.

Another difficult question to decide is, how far surface forces, adsorption, etc., have to be taken into consideration in the case of colloidal electrolytes. There is strong evidence that we are right in doing so in very many cases. That different parts of large molecules have different functions is acknowledged fairly generally. It is therefore quite possible that, in soap solutions for instance, the carboxyl groups, being dissociated, are mainly responsible for the electrical properties of the solutions. But there are large regions, the surface of the long chains, which have a totally different nature and being strongly hydrophobic are capable of causing a marked adsorption. It is most probable that the different parts of the molecular surface will influence one another to a certain extent and so the electrical properties will not remain quite unchanged in presence of strongly adsorbable substances.

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**Professor E. J. Bigwood** (*Brussels*) then said : At the end of his report, Professor Freundlich mentions that on the whole, the particle size of colloidal electrolytes is not so very great ; the molecular weight ranges as a rule between a few thousands and some 100,000. It should be remembered, however, that amongst the proteins which are to be considered as colloidal electrolytes, there are some of exceedingly high molecular weight reaching several millions, such as hemocyanine for example.

**Professor Wo. Ostwald** (*Leipzig*) said : Professor Freundlich gave in his introductory paper a condensed historical survey of the development of the conception " colloidal electrolytes." May I give here a short addition, which may be of some interest. In 1909 J. Duclaux compared, as Freundlich points out, some colloids with ordinary electrolytes. But only one year later, 1910, obviously quite independently of Duclaux, somebody else in England and in English words introduced the same conception into British science and coined a special expression, calling those sols " electrolytic colloids." This author even published a whole paper with the title " Electrolytic colloids." To quote from this paper :

" When the relatively immobile constituent in a colloidal solution is an ion, electrolytic phenomena will occur at internal surfaces. Such cases form special developments of ordinary electrolytic solution and may be classed as *electrolytic colloids*. When the immobile constituent is a neutral substance, we have a second class related to ordinary nonelectrolytic solution and therefore to be called *nonelectrolytic colloids*.

As examples of the former class may be taken metals, soaps, hydrosul-
phides, and certain proteins in water.    And of the second, agar or gelatin
in water, or celloidin in ether and alcohol."

This paper, it is true, has probably not been read by many, because
it appeared in a memorial volume dedicated to the Dutch colloid chemist
J. M. van Bemmelen in 1910.

The author who most clearly gave quite independently of Duclaux and
at about the same time this fundamental conception was William B.
Hardy.

Please allow me at the beginning of this meeting to recall in this way
the memory of this truly great and beloved spirit.

# PART I.  GENERAL : (A) THEORY.

## SOME RELATIONS BETWEEN ELECTRO-CHEMICAL BEHAVIOUR AND THE STRUCTURE OF COLLOIDS.

By WOLFGANG PAULI.

(*Translated by* Dr. HENRY V. B. BULL.)

### 1.

The recognition of the importance of the electrical charge for the stability of colloids (the foundations of which were laid by the brilliant English worker, W. B. Hardy, who recently passed away), soon necessarily lead to the question as to the origin of the charge on the colloid particles.   But the answer to this question did not appear very urgent to many workers so long as the Quinke-Helmholz picture of the electrical double layer was capable of explaining many of the properties of the colloid particle.   The assumption of the ionic origin of the particle charge and the often successfully used adsorption idea is responsible for the conception that the adsorbed ions, which cause the charge on the particle, exist on the particle surface as point charges.   This assumption of a charging ionic adsorption has been used by some workers for a long time and its use continues to-day.   An adsorption of oppositely charged ions of an added electrolyte on these point charges should cause the discharging and finally the flocculation of the colloid.

Gradually a more chemical point of view had to be assumed, as it turned out that in many cases the surface of the colloid particle showed in no way the chemical reactions of an elementary ion which gives rise to the charge but rather that of a definite compound of it.   For example, an $As_2S_3$ sol does not obtain its charge from sulphide ion, as was earlier assumed, but from the complex arsenious sulphide ion.[1]   In other cases it was found in certain coagulation processes, for example, with freezing or boiling of the noble metal sols that this was accompanied by separation not of single ions but of higher complex ions with a metallic central atom.   There are cases, for example, where the positive metallic oxide sols on dilution do not lead to simple ions, which give rise to the charge, but to an acid as a typical product of salt hydrolysis.   In other cases, without exception, so far as we have been able to determine, all originally non-acid negative colloids, upon dialysis or electrodialysis, show as a very characteristic effect an exchange of the *Gegenions* for the H ions. The sol is changed into an acidoid.   We must regard this typical behaviour as a salt hydrolysis where the complex anion remains fixed on the surface of the particle.   When we consider, in addition, such organic

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[1] Pauli and A. Semler, *Kolloid Z.*, **37**, 145, 1927 ; A. Semler, *Kolloid Z.*, **37**, 209, 1927.

and inorganic sols on the one hand as congo dyes, " night blue " (*Nacht blau*), gum arabic which have been prepared in the purest state, and on the other hand, for example, the silicic acid and tungstic oxide sols, which show clearly defined ionogenic complexes, we then recognise the advantage of a unified theory of the origin of the charge of the colloid particle by means of an ionogenic complex attached to its surface.

This theory has recently proved satisfactory in an especially difficult case, namely, colloidal gold. Colloidal gold was long regarded as purely metallic and accordingly the particle charge was considered to arise from the ionisation of the metal in the same manner as a Nernst electrode. Another deciding point in favour of our theory was that wide differences were detected in the behaviour of sols of the same kind. These differences could only be explained on the basis of differences in structure of the charge complex on the particle surface. So gradually the chemico-structural point of view came to have a meaning for the understanding of reactions of a colloidal type which up to this time had been considered only in relation to the size and shape of the particles, as well as the number, density and distribution of charges.

## 2.

Let us now consider the manner, and what in many cases is almost the same, the difficulties of determining the ionogenic complex in a sol. It is necessary in critical cases to have great purity and high concentration of the sols. It can then be assumed that the sol contains only the colloidal ions and their *Gegenions*. This goal has hitherto been reached in relatively few cases and only then through electrodialysis (E D) * and a variety of the same, electrodecantation (E Dek). By means of E D silicic acid and a series of dye sols, protein sols, and also plant colloids (such as starch and gums) have been prepared in a pure state. In addition we have in our Institute by means of E Dek purified and concentrated gold, silver and platinum sols, as well as ferric oxide sols. Lately Verwey and H. R. Kruyt [2] have in like manner prepared a silver iodide sol.

In the E Dek as we have developed it the electrical separation of the electrolyte plays only a small rôle. The current serves above all to concentrate the sol by forming a layer by electrophoresis. The sol is then washed with pure water as with simple decantation. This process is repeated many times. An electrical potential of 2 volts can be used, and in general the potential need not exceed 10 volts. When this method cannot be used purification can be achieved under certain conditions, for preliminary studies, by means of dialysis, or by preparing the sols over organic solvents. Dialysis at higher temperatures cannot be used for our purposes because impurities are given off from the membranes which completely change the sol.

The ideal way would be to separate the unchanged ionogenic complex from the colloid particle and to determine its constitution. In certain cases this method cannot be directly used because of the relative instability of the complex. A certain amount of evidence can be obtained from the study of the decomposition products or the reconstructed complex. As has already been said an acidoid is formed on the typical

* Throughout this paper we shall refer to electrodialysis as E D and to electrodecantation as E Dek.

[2] *Z. physik. Chem.*, **167A**, 179, 1933.

hydrolysis of a negative sol with ionic exchange. This appears to us to be a good argument for the existence of an ionic complex on the sol, and this changing of the gold and silver sols into acidoids has served as the first link in the proof of the existence of this ionic complex. A further hydrolysis of the complex acid leads, for example, with $[PtCl_4]H_2$ to $[PtCl_3OH]H_2 + HCl$. Differences in the ease of association of OH ions to the central ion of the complex can give us considerable insight into the properties of the sol. It can be shown by conductometric $H^+$ on titration of the auric acid chloride that the first Cl of the complex can easily be completely substituted, while the other can only be displaced at high OH activity. Accordingly we write the equation

$$(AuCl_4)H^+ + 2NaOH \rightarrow (AuCl_3OH)Na + NaCl$$
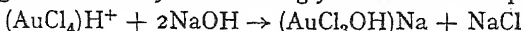
Two equivalents of base are needed for one equivalent of auric acid chloride. This result was important in the analysis of the gold sol. It appears indeed that it can be used for some other ionogenic complexes and it is of value for reference purposes.

This is an example of the beginning of the reconstruction of a complex containing anions all of the same kind into a mixed complex. This mixed complex, through a complete change of the anions, then becomes again a homogeneous complex. Accordingly in the presence of an excess of base a pure chloro- is changed into a pure hydroxo-gold complex. The accompanying change in the colloidal behaviour with such a reconstruction is of great importance, and can be explained by structural chemical relations. The testing of the reversibility of the constitutional and, parallel, colloidal changes from this point of view often clarifies the situation. Such an investigation often discloses connected secondary reactions; for example, the transformation of a metallic hydroxide into a more dehydrated compound.

The simple splitting and the reconstruction of the complex are important processes for the conditions of the particle charge and the reactions on the colloidal surface. For example the reconstruction of a complex by reactions of the following type

$$Au(OH)_3 + NaOH \rightleftharpoons [Au(OH)_4]Na.$$
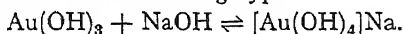
The manifold changes of the complexes will be illustrated as far as space allows.

## 3.

In addition to the ionogenic complex which gives rise to the charge on the particle there exists a neutral part which is practically non-dissociated and which often constitutes the larger part of the composite colloid. This neutral part to which the ionogenic complex is attached can have a number of relationships to the ionogenic complex and influence its properties in a number of ways. All grades of relationships can exist; from chemical identity and differences due to ionisation (as with the soaps and certain dyes) to molecular rearrangements (as with congo blue), and further to almost complete differences of the neutral part from the ionogenic part as with the noble metals. In addition to this we have the not unusual case of several kinds of neutral parts existing together; this, on the one hand, influences the adhesion of the ionogenic fraction through the lattice forces and, on the other hand, it can to a certain extent influence the surface reactions of the colloid particle.

Only a short discussion of the difficult but very important problem of the influence of the ionogenic complex through the neutral part of

the colloid can be given.  We have repeatedly found that a negatively charged colloid complex with $H^+$ as the *Gegenion* is extremely stable, while as an acid in the free condition it is practically completely decomposed.  An example of this kind is the sulpho-arsenic complex on an arsenic tri-sulphide sol, which exists as $As_2S_4H_2$ and when isolated splits into $As_2S_3$ and $H_2S$.  Another example is the silver sol with $AgCl_2^-H^+$ as the ionogenic complex, which under certain conditions is very stable. In this case the addition of small amounts of HCl to AgCl in an aqueous medium does not increase the solubility by building a complex but decreases it.  The aurochloric acid $(AuCl_2)H$, which is the ionogenic complex on the very stable Bredig gold sol dispersed in HCl, decomposes immediately when separated from the gold and in free condition to Au, HCl and $H(AuCl_4)$.  The reciprocal reaction between the neutral part and the ionogenic complex is strikingly shown in the following cases. It is not possible to prepare a stable silver sol by dispersing silver in pure water.  Owing to a small amount of electrolysis, however, a silver oxide is produced after a time and because of the solubility of the $Ag_2O$ (which in turn gives rise to the strong base, AgOH) a rapidly increasing silver sol concentration is obtained.  If the dispersion is made with AgOH already present a dispersion sol is formed immediately.  This was shown by V. Kohlschütter.[3]  It is worth noting that in such negative silver sols $Ag^+$ is the only ion which can be regarded as the *Gegenion*.  The Ag ion can be exchanged for $H^+$ ions under the proper conditions as with all silver sols.  This can be brought about by dialysis or, as Kohlschütter[3] has done, by reduction with $H_2$ in a platinum dish.  We can consider in this case only one $AgO^-$ or an analogous "argentate" as the negative ionogenic complex, and we see that this $AgO^-$ is in ionic equilibrium with either $Ag^+$ or $H^+$ and does not form $Ag_2O$ or $Ag^+OH^-$, as might be expected.

The factor which all the examples given appears to us to have in common is the following.  The ionogenic complex on the sol appears to be firmly attached in the first shell.  The anions are bound to the positive central ion, at the same time, however, the dissociation of the $H^+$ ions is increased.  One can view the matter in the same sense as W. Kossel has done.  On the one hand the attractive force of the central metallic atom is increased for the anions in the first shell, and on the other hand the repulsive force for the outer cations is increased.  It is as if the central positive charge of the complex were augmented.  Such an enlarged electrostatic effect is conceivable when the central field arises from more than one metallic ion.  This increase could take place from the combination of two or more heteropolar molecules, in which perhaps $Ag_2O$ reacted together with AgOH in such a fashion that in an average time a higher * complex would be present, for example.

In an analogous manner it is possible that we can have stable combinations such as $[As_2S_3 . As_2S_4]H_2$ or $[As_2O_3 . As_2S_4]H_2$ and further $[AgCl . AgCl_2]H$, $[AuCl . AuCl_2] . H$.  The co-operation of the ionogenic complex with a heteropolar molecule permits us to understand and to unify the facts of the



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[3] *Z. Elektrochem.*, **17**, 43, 1908.

* Here we have expressed in a schematic manner a purely complex chemical representation of the reactions of neighbouring heteropolar molecules in the crystal lattice of the colloidal surface.  This representation can express only approximately the actual relations.
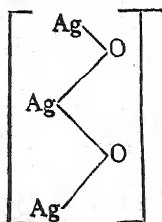
increased positivity. This seems, for the time being perhaps, preferable to a special explanation for the noble metal sols, where we would suppose a direct influence of the ionogenic complex on the metallic atoms of the lattice. The necessity for the fitting together in the space lattice of the
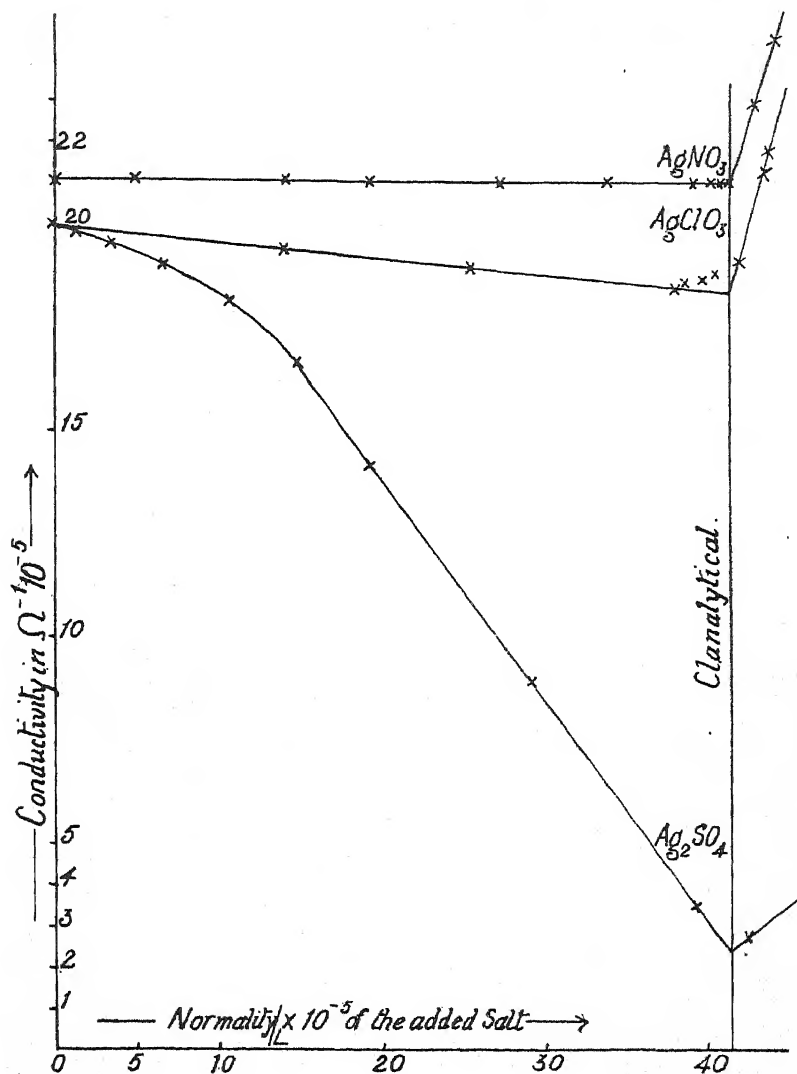


FIG. 1.—Aluminium oxide sol.

different neutral parts as well as the neutral part with the ionogenic complex in the colloid particle has been discussed earlier. In this connection we can only briefly give a meaning to the identity of the central atom, the capacity to form mixed crystals (for example the ability of Au and Ag to form nucleus-sols), the rôle of the valency of the central atoms

where the lower valent metallic ion is related more closely to the elementary atom and has therewith a greater capacity for adhesion.

It is to be expected, in analogy to the increased effect of the central ion on the associated ionogenic complex of negative colloids, that such a relation would also be found with positive colloids. For example, an increased positivity of the ferryl- or aluminyl ion which gives rise to the charge could, in sufficiently pure iron oxide or aluminium oxide sols, enhance the inactivation of the negative *Gegenions*. At this stage it
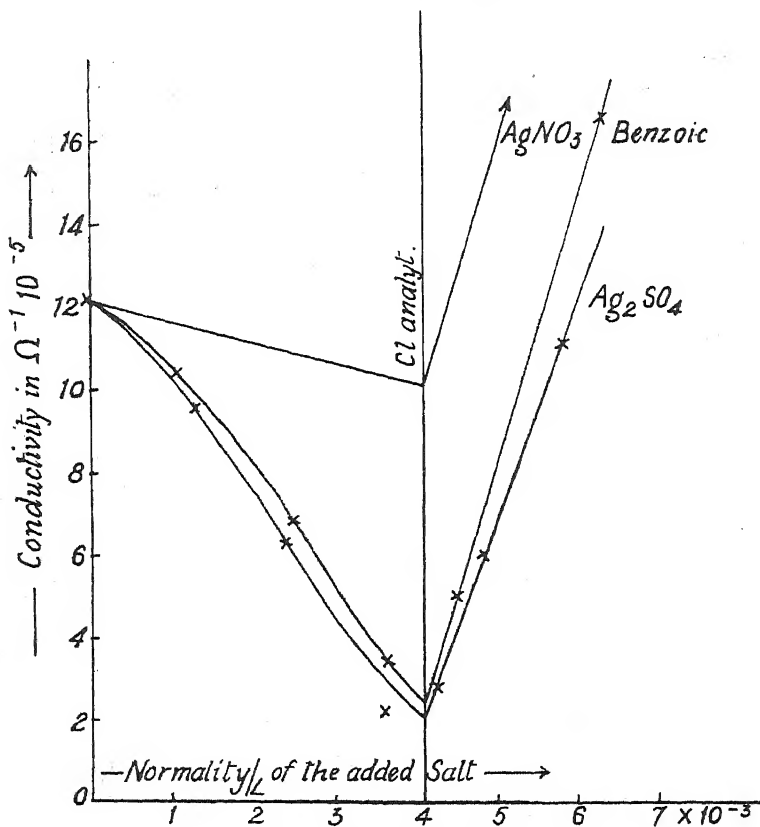


Fig. 2.—Thorium oxide sol.

is perhaps relevant to mention that with these sols the bivalent sulphate ion becomes completely inactivated and that there is a difference in the action of the bivalent cations with negative colloids, since an excess of $SO_4$ ions is not required for flocculation. As was first shown by J. Duclaux[4] sulphate ions in equivalent concentration displace the opposite Cl ion of the metallic oxide sol and discharge the sol completely.[5] This is remarkable, because the free Fe- and Al-sulphates are readily soluble compounds. It will be necessary, therefore, in order to explain such increased interionic effects on sol particles with the polyvalency of colloid

[4] *J. chim. physique*, **5**, 29, 1907.
[5] Pauli and J. Matula, *Koll. Z.*, **21**, 49, 1917; Pauli and G. Walter, *Koll. Z.*, **17**, 256, 1923; Pauli and F. Rogan, *Koll. Z.*, **35**, 131, 1924.

ions to consider also a formation of the higher complexes on the colloid surface, between the neutral part and the charged ionogenic group (for example $Fe(OH)_3$ and $FeOCl$).

The substitution of the trivalent Al or Fe in their metallic oxide sols by tetravalent Th (in thorium oxide sols) shows markedly the greatly increased inactivation of the *Gegenions* through the stronger positivity of the central atoms of the ionogenic complex. Here we already see that the difference in behaviour of the univalent ions with eccentric charge (as $NO_3$, $ClO_3$), as compared with the inactivation of Cl, is very noticeable. This is shown by Figs. 1 and 2, which illustrate the method of *Gegenion* exchange [6] in Al- and Th-oxide sols [7] containing the chloride ion, where a *Gegenion* is brought about by means of the corresponding silver salt.

### 4.

The theory of a charge arising from an ionogenic complex appeared to meet with great difficulty with the noble metal sols and especially with colloidal gold, their chief representative. These sols have, however, through the researches of recent years developed into the best examples of the connection between collodial behaviour and the structure of the complex. To be sure we cannot go into the many highly interesting details, and we must content ourselves with a consideration of the general relations.[8] The use of the classical Bredig's method for dispersion suggests itself as the simplest way for our purposes. The dispersion must take place in HCl,[9] so that a gold chloride is formed on the gold particles from the $Cl_2$ produced by electrolysis, which in the presence of HCl goes to auric acid chloride. The first process takes place only during the dispersion, the second lags somewhat, so that in the first twenty-four hours the conductivity and hydrogen ion activity of the sol due to the taking up of HCl can fall to a half or less. When the dispersion takes place in alkali a pure hydroxo-complex is obtained on the gold, by combination of the electrolysed nascent hydroxide with the alkali according to the following reaction:

$$Au(OH) + NaOH \rightarrow [Au(OH)_2]^-Na^+$$
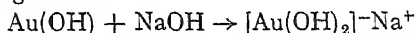
We can determine the ability of an anion to form an ionogenic complex by varying the dispersion medium (as H. T. Beans and H. Eastlack [10] have done), or by the subsequent addition of an anion to a sol which has been prepared with insufficient electrolyte [11] [OH, Cl, and Br give rise to complexes, $NO_3$, $SO_4$, $HCO_3$, $CO_3$, $S_2O_3$ are unsuitable].

There is a real difference between gold sols with hydroxo and those with halogenic complexes.[11] It has been subsequently found that the characteristic peculiarities of the negative hydroxo sols are found in a great many sols other than those of the colloidal noble metals.

Hydroxo-gold sols are distinguished from the chloro-gold sols by being precipitated when $CO_2$ is passed into the sol, and also on boiling. In the first case the ionogenic complex is destroyed by the formation of a

[6] Pauli and E. Valkó, *Z. physik. Chem.*, **121**, 161, 1926 ; *Elektrochemie der Kolloide*, Wien, 1929.

[7] Pauli and E. Schmidt, *Z. physik. Chem.*, **129**, 199, 1927 ; Pauli and A. Peters, *Z. physik. Chem.*, **135**, 1, 1928.

[8] See Pauli, *Naturwissenschaften*, **20**, 551, 573, 1932.

[9] Pauli and F. Perlak, *Koll. Z.*, **39**, 196, 1926.

[10] *J. Amer. Chem. Soc.*, **37**, 2667, 1915.

[11] F. Eirich and W. Pauli, *Koll. Beih.*, **30**, 113, 1930.

bicarbonate which cannot give rise to a complex.  By boiling, on the other hand, the complex is hydrolysed, and an insoluble anhydride form of the oxide such as $Au_2O$ is formed.  This hydrolysis and irreversible change is hindered by excess of alkali.  Only the halogeno sols are stable in air $(CO_2)$.  By electrolysis the alkali is removed from the hydroxo sols and they are quickly flocculated.  In contrast to this the halogeno sols can be electrodialysed [8, 12] and only after a protracted E D is the sol converted into a hydroxo sol and finally precipitated.  The change from chloro sol to hydroxo sol can at any time be brought about by the addition of alkali, and is completely reversible with HCl giving the behaviour of the original sol.  Since it competes with the $Au^+$ for the $OH^-$, $Ba^{++}$ is much more effective as a flocculating agent for hydroxo sols than for chloro sols.[13]  The threshold value for rapid coagulation with $BaCl_2$ is five times smaller in the first case than with the last, that is $4 \times 10^{-5}$ $n$.

The variety of reactions of gold sols with different structures of the ionogenic complex is extraordinary.[13]  We will discuss here briefly only the behaviour of the sols on freezing, because it throws light on the stability of the ionogenic complex.  Highly purified gold with a concentration of 5 grams per litre or more can be prepared by means of electro decantation of a sol dispersed in HCl.  Such a sol is completely coagulated upon freezing.  This can increase the conductivity threefold because of a higher [12] titratable $H^+$.  The higher electrolytic concentration obtained by freezing and coagulation distributes itself between HCl and $[AuCl_4]H^+$.  Moreover, when the HCl obtained from the freezing of the sol is considered a ratio of 2 : 1 is obtained for the relation of increased HCl to $H[AuCl_4]$.  This is true for the less purified as well as for the highly purified sol.  This ratio corresponds to an auro-auric equilibrium as first formulated by Wohlwill : [14]

$$3(AuCl_2)H \rightarrow 2Au + 2HCl + (AuCl_4)H$$
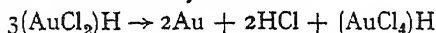
The ionogenic complex separates from the gold sol because of the higher concentration of the chloro-gold sol obtained upon freezing.  This process continues for eight to ten days if the liquid is allowed to remain in contact with the coagulum.  A further increase of about 16 per cent. in conductivity is obtained.  This process can be accelerated by boiling.  All the observed phenomena can be explained by considering the disintegration of an auro chloric acid which separates from a gold sol.  This auro chloric acid is, however, quite stable on the sol particles.

By progressive E Dek of chloro-gold sols a mixed complex [AuOHCl]H is obtained.  Upon freezing, this complex gives up equivalent quantities of H and Cl according to the following equation :

$$3[AuOHCl]H \rightarrow Au(OH)_3 + 3HCl + 2Au.$$
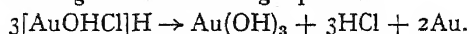
If the pure chloro-gold sol is recovered from this sol by the addition of HCl it is found that, in all, four HCl are needed, and this HCl combines to form $(AuCl_4)H$ which appears in the liquid which had been frozen.  This can be exactly demonstrated by a $Cl^-$ titration after the reduction of the complex.[15]

The separation of the ionogenic complex through freezing is connected with the inactivation of the *Gegenions* as a result of the high concentration of the sol.

[12] Pauli and Ed. Russer, *Koll. Z.*, **58**, 22, 1932.
[13] F. Eirich and W. Pauli, *Koll. Z.*, **67**, 186, 1934.
[14] *Z. Elektrochem.*, **4**, 379, 402, 421, 1897 ; **9**, 315, 1903.
[15] Pauli and Ed. Russer, *not yet published*.

The process is somewhat complicated. On the one hand, the mutual approach of the discharged gold particles makes the lattice forces between the neutral parts of the same effective. On the other hand, the attachment of the *Gegenions* produces a contrapolarisation (V. Goldschmidt) in the anionic co-ordination shell of the complex. It becomes entirely dependent on the ratio between the work of separation of the entire ionogenic complex and the energy required for the splitting of the complex itself. Both cases are found in the concentration of the sols by freezing. Thus, the complex $[AuBr_2]H$ is more readily split into the insoluble AuBr and into HBr in analogy to the chloro-hydroxo-mixed complexes, while the pure chloro-gold complexes are almost entirely separated from the gold accompanied by dismutation.

## 5.

In some ways the behaviour of platinum sols is different from that of the gold sol. Because of the more strongly acid nature of the platinum oxide it is possible to disperse the Pt in pure water as the hydroxo sol with $H^+$ as the *Gegenion*. The fundamental work on these sols was done by S. W. Pennycuick.[16] This work was planned on the basis of the theory which we give here. Pennycuick showed that with this Pt sol we have to do with two kinds of reactions on the surface of the particle ; on one hand with the *Gegenions* of the ionogenic complex which are exchangeable with the added cations, and on the other with the reactibility of the non-ionising oxide, which reacts like an acid anhydride with bases and sets free the acid formed by the taking up the base formed by the hydrolysis of the added salts, whereby a new ionogenic complex is formed. The hydroxo sol of Pt coagulates upon freezing without an increase in the conductivity. A complex acid of Pt, which in the sense of Pennycuick is probably the hexahydroxo acid, can be detected in the liquid which had been frozen. A large increase in the conductivity and the titratable $H^+$ is obtained, upon boiling, in the sol as well as in the liquid which had been frozen. In the oxide-poor sols (prepared in a stream of nitrogen) prolonged boiling leads finally, with release of the acid, to coagulation. At the time of Pennycuick's experiments it was not known that it was possible to suppose a dismutation of a compound of lower valency of the metal accompanying the separation of the complex. He therefore regarded the liquid which had been frozen as the unchanged dispersion medium of the sol. After our experience with gold it appears however that the observations on freezing and boiling of the Pt hydroxo sol may be connected with the formation of secondary products as a result of the decomposition of a platino oxide acid. A decision cannot at present be made.

In general the chlorosols furnish, as a result of the possibility of chloride titration, with and without reduction of the complex, more evidence of its constitution than hydroxo sols. We have therefore undertaken experiments * in which the chlorosol of Pt is prepared by dispersion in HCl. The sol is purified and concentrated by means of E Dek. The sols are very sensitive, and therefore the electrode potential cannot exceed 2 volts. We succeeded in this way in attaining a concentration of 2 gr. of Pt per litre. The sols obtained had a relatively large amount of

[16] *J. Chem. Soc.*, 2600, 1927 ; 551, 1928 ; *Koll. Z.*, **49**, 407, 1929 ; *Z. physik Chem.*, **178A**, 413, 1930.
* With Th. Schild ; *not yet published.*

titratable $H^+$ and no titratable Cl.   Upon freezing the conductivity and $[H^+]$ in the majority of cases were decreased somewhat, and at the same time titratable Cl appeared in the liquid which had been frozen. Pt is detectable only in traces (about $2 \times 10^{-6} N$) and the titratable Cl is increased only a few per cent. by reduction.   It is therefore mainly HCl accompanied by very small amounts of a chloro-platinic acid which is set free upon freezing.   On the other hand about one-third of the total Cl can be obtained from the washed coagulum (obtained through freezing) by means of reduction.   The ratio of H to Cl varies from 1 : 2 to 1 : 3. Almost exactly twice the amount of $H^+$ can be titrated with barium hydroxide as with NaOH.

All these observations appear to be best understood if we suppose that an ionogenic complex, $[Pt(OH)_2Cl_2]H_2$ or $[Pt(OH)Cl_3]H_2$ is present in a Pt chloro sol, and that this complex can easily be obtained through the hydrolysis of the platino hydrochloric acid.   This complex is split up on freezing, as a result of the insolubility of the platino oxy-chloride with release of HCl and is only to a very small extent dismutated. The ease of the splitting of the complex permits—as with bromo gold sols—only an extremely careful use of E Dek.   Up to the present the investigations on Pt sols have brought us only a few sure steps into a field of particular importance for catalysis.

The silver sols [17] obey the same laws as the other noble metal sols as far as they are determined by the structure of the ionogenic complex. The pure hydroxo silver sols prepared in alkali or ammonia are extremely sensitive to $CO_2$ and E D and precipitate also on standing in the air. Contrasted with this behaviour the chloro silver sols prepared in the purest dilute HCl are resistant to $CO_2$ and can be purified and concentrated by means of E Dek.   The sols dispersed in alkali chlorides have a mixed complex and occupy a middle place in behaviour.   They are indeed sensitive to $CO_2$.   They can however be purified by careful use of E D and are in this way transformed into the acidoid.   The peculiarities of the Ag sols are to be seen particularly in formation of molecularly dispersed AgOH along with the sol and in addition in the reaction with ammonia, which results in the complex *Gegenion* $Ag(NH_3)_x$.   This complex has a stabilising action on the sol.   A further peculiarity is the high sensitivity to light.

## 6.

In connection with the above discussed relations between colloidal changes in condition and the constitution of the ionogenic complex it is of interest to follow these relations with the changes of structure which accompany the reversal of charge of colloids in the phenomenon known as the " irregular series."   We wish to follow this through by means of the highly purified iron oxide sol as an example.   We have made (with Dr. H. Neurath) a long series of experiments for this purpose.[18]

An iron oxide sol produced by boiling of a dilute iron chloride solution can be highly purified and concentrated by repeated E Dek.   One obtains in this manner a splendid, completely stable neutral sol with constant conductivity of $2 - 5 \times 10^{-6}$ reciprocal ohms and a $p_H = 6\cdot8$. It contains practically only the positive colloid ions and the Cl *Gegenion*. As the source of the charge we can consider only one univalent ion

[17] J. Löffler and Pauli, *Koll. Z.*, **60.** 176, 1932.
[18] *Z. physik. Ch.*, **163A,** 351, 1933 ; *a further communication in hand.*

$FeO^+$ or $Fe(OH)_2^+$. The sol is coagulated in lumps by boiling or by shaking and leaves a red liquid which contains finely dispersed colloid particles. The conductivity and chlorine content are thereby tremendously increased even though the reaction remains completely neutral. Upon freezing the sol is completely coagulated in the form of silk line crystals with the release of HCl, which is shown by the increased conductivity as well as the $H^+$ and $Cl^-$ activity in the water clear liquid after the freezing. The ionogenic complex is decomposed by hydrolysis following the crystallisation of the concentrated sol, which had been frozen.

Such highly purified iron oxide sols become by high concentration of salts with tetra-valent anion $K_4FeCy_6$ or $Na_4P_2O_7$ oppositely charged into a clear negative sol. This change is however not brought about by the trivalent anions such as $K_3FeCy_6$. The sol is flocculated in the lower concentration of these salts. We cannot disperse this coagulum into a negative sol by the further addition of tetra-valent anions. The reversal of the charge of our iron oxide sol cannot therefore be brought about by the addition of the required amount of the tetravalent anion in fractions. It must all be added at one time. The ionogenic complex becomes blocked upon the addition of flocculating amounts of the tri- or tetra-valent anions, and a further entrance of anions is not possible. Other observations show that with iron oxide sol practically an equivalent amount of the chloride *Gegenion* is set free upon the addition of a polyvalent anion and only a small amount of $OH^-$; which increases the $p_H$ somewhat. The polyvalent anion react principally with the ionogenic complex, e.g., with $Fe(OH)_2^+ Cl^-$, not however with a neutral oxide on the surface of the particle. It appears to us to follow from the impossibility of charge reversal with the trivalent anions that the reaction does not occur through a bridge-like combination of three neighbouring $Fe[OH_2]^+$ but in the sense of the following reaction

$$Fe(OH)_2 Cl + K_3 FeCy_6 \rightarrow Fe_3 FeCy_6 + 2KOH + KCl$$
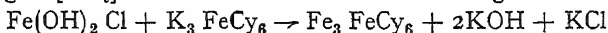
The liberated OH ions would immediately enter into the neighbouring ionogenic complexes and displace Cl ions. This would also be the chemical picture * of a polarised surface produced by a colliding polyvalent anion. The reversal of charge through tetra-valent anions (type I) as shown by pyrophosphate can be imagined to take place by means of a reaction with the ionogenic complex in the following manner:

$$Fe_3(OH)_2Cl + Na_4P_2O_7 \rightarrow [FeP_2O_7]^- Na^+ + 2NaOH + NaCl$$
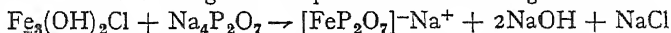
The reconstruction of the ionogenic complex by means of basic or alkaline hydrolysing salts, e.g., with trivalent anions such as phosphate or citrate, provides another type. It has been shown that here the reversal of charge (type II.) always results with an excess of OH groups, whereas at lower concentrations the discharging by means of OH takes place with the salts with high valent anions through the simultaneous action of the anions. The model for this discharging and reversal of charge is found in the transformation of a hydroxide into a ferrate. For example

$$Fe(OH)_2Cl + KOH \rightarrow Fe(OH)_3 + KCl$$
$$Fe(OH)_3 + KOH \rightarrow Fe(OH)_4^- K^+.$$
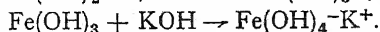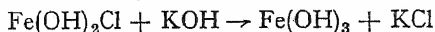
The reversal of the charge by such electrolytes (which will be referred to in an abbreviated form as " OH group ") results also in flocculations with tri- or tetra-valent anions of neutral salts; for example potassium

ferri- or potassium ferro-cyanide.  This reversal of charge is also pro-
duced with all flocculations brought about by single members of the
" OH group " with the addition of the same or other members of this
group.  The freshly formed negative complex can show all variations
between $[Fe_3(OH)_4]^-$ and $Fe_3[An_3OH]^-$.  Since this new hydroxo com-
plex was formed out of the original ionogenic complex of the positive
sol and not from the neutral oxide on the particle surface it follows that
the reversal of charge of a ferrocyanide precipitate by means of the
entry of OH is prevented through a further addition of ferrocyanide.
With sufficient addition of OH the $FeCy_6$ is displaced and, on the other
hand, the entrance of OH into the complex is hindered by an excess
of $FeCy_6^{----}$.  All the effective ions have one and the same point of
attachment, the ionogenic complex of the original sol.  This is to be
expected from the method of preparation of our sols and the refractory
behaviour of their oxides with acids and alkali.

The sols, whose charges are reversed in the manner of type I. (with
$FeCy_6^{----}$ or $P_2O_7^{----}$), can be distinguished in a characteristic fashion
from those of type II.  Only the latter negative sols are flocculated with
$CO_2$; the former are completely stable with $CO_2$.  This behaviour re-
minds one exactly of the difference between the halogeno- and hydroxo-
noble metal sols.

The flocculation of our negative hydroxo sols of type II. is produced
by addition of equivalent amounts of acids of different strengths.  The
flocculation depends in this case upon a neutralisation of the excess
OH-groups in the ionogenic complex.  On the other hand, our negative
sols whose reversal of charge belongs to type I. are coagulated only
by a high acid concentration.  Since in this case the flocculation takes
place through the increase of H ions in the *Gegenion* atmosphere of
the colloid particle, the $H^+$ activity, that is, the acid strength, is
important.

Finally, it is possible to reconstitute the original positive sol out of
the negative hydroxo sol, whose charge has been reversed, by the con-
tinuous addition of a strong acid with a univalent anion.  At first there
is flocculation through neutralisation, and with the right amount of acid
we obtain complete peptisation to a positive sol.  Accordingly a rever-
sible cyclic process on the ionogenic complex is also possible here, as
between hydroxo- and chloro-gold sols, with the difference, however,
that in the last case the total anion exchange is confined to the first
co-ordination sphere of the complex and, also, that a change of the sign
of its charge does not occur.

## 7.

We now desire to turn to some examples of organic sols which give
us considerable knowledge concerning the relation between the structure
and the electrochemical and colloidal behaviour.  The proteins, the
soaps, and the starches will be disregarded because detailed monographs
have been written about these substances.

A pure acidoid, the physico-chemically well-defined congo blue is
obtained by complete electrodialysis of congo red.[19]  The blue quinoid
*zwitterionic* form may be regarded as the neutral part of this sol.

[19] Pauli and E. Weiss, *Biochem. Z.*, **203**, 103, 1928 ;  Pauli and L. Singer,
*Bioch. Z.*, **244**, 76, 1932.
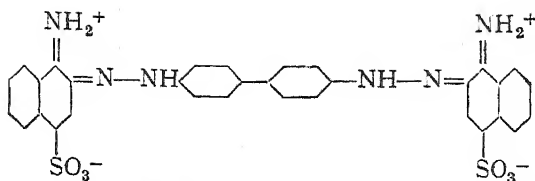
I. Blue quinoid form.
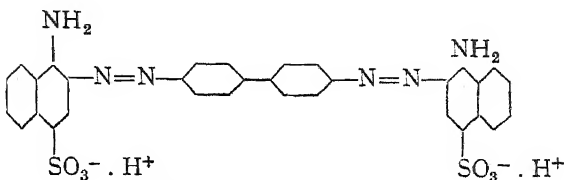


II. Red azoid form.

## Congo-Red.

We have to deal here with two strongly acidic sulpho groups on the one side and, on the other, with two weakly basic amino groups. The partial hydrolysis of the amino groups by alkali produces a rearrangement into the azoid, negatively charged, red form (II.) out of which the congo red is entirely composed. In our congo-blue sol the red form constitutes the ionogenic complex with $H^+$ as the *Gegenion*. The hydrolysis of the *zwitterionic* form must be regarded as the origin of the negative charge of the sol, as is also the case with the purest albumin. From this there are derived a series of relations between these two, otherwise so widely different *zwitterionic* sols and, in addition, a number of characteristic differences, which appear to be constitutionably understandable.[20] The colour change from blue to red is accompanied by a decided change in the size of the dispersion. This, however, is not the cause of the colour change, which occurs in the same manner as that of the crystalline amino sulphonic acid, methyl orange,[21] namely, by an intra-molecular rearrangement of the quinoid $\rightarrow$ azoid type. The blue *zwitterionic* form associates to a greater extent than the polar red form.

The difference in dispersity is an accompanying secondary phenomenon of the change in constitution. The congo-red forms particles which are related to the ionic soap micelles of McBain. The congo-blue, on the other hand, resembles more closely inorganic lyophobic sols. Heating of the congo-blue sols increases the hydrolysis of the amino groups, and augments the polar form at the cost of the *zwitterionic*. With hydrolysis the total free charge is increased, the colloid equivalent is diminished (the colloid equivalent $K$ is the number of molecules per free charge) and finally a change into the red colour takes place. Carbonic acid favours the *zwitterionic* form (by forming an imonium bicarbonate). The conductivity increases upon heating out of proportion to the temperature and remains high upon cooling as a result of the loss of $CO_2$ and the disaggregation of particles.

The congo-rubin sols (studied by Wo. Ostwald in a series of important researches in respect to their dispersivity and colour changes) can be

[20] Pauli, *Koll. Z.*, **51**, 27, 1930 ; *Trans. Far. Soc.*, **26**, 723, 1930.
[21] F. W. Küster, *Z. anorg. Chem.*, **13**, 135, 1897 ; *Jahrb. f. Chem.*, **7**, 64, 1898.

completely transformed into the azoid form by means of E D.[19]  Its behaviour can also be constitutionally understood.  Only one half of the molecule has, however, an amino group.  Only this part of the congo-rubin molecule is capable of a *zwitterionic* (quinoid) → polar (azoid) rearrangement.



III. Congo-rubin.



IV. Congo-corinth, blue, quinoid.
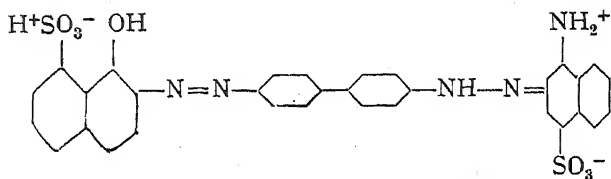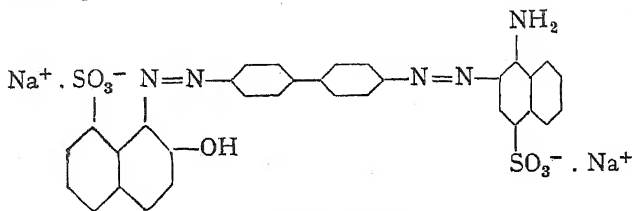
The other half of the molecule has the second sulphonic group next to a phenolic hydroxyl group.  Accordingly the acid character is noticeably strengthened, the basic becomes weaker and a large part of the molecules are transformed into the pure polar anionic red form as an effect of hydrolysis.  There results a higher total charge and conductivity, as well as a smaller colloid equivalent.  Thus there results for a congo blue sol of $3 \times 10^{-4}$ molar, $K = 17$ to 18 dye molecules for each free charge, while for a like concentration of blue congo-rubin sol $K = 2$. There is always a free finely dispersed red part in equilibrium with the coarser blue particles.  The hydrolysis is from the beginning so high that the increase of the conductivity with temperature can be expressed as only an approximately linear relation, and the favouring of the *zwitterionic* form through $CO_2$ is largely prevented.  Congo-corinth (an isomer of congo-rubin) shows, as a purified acidoid sol, a strongly increased acid character as a result of the close proximity of the acid OH-groups to sulphonic groups.  The basic groups are still further weakened.[22]  Therefore the polar form is still further favoured, and a well-conducting ionic micelle is obtained.  On the other hand, the Benzopurpurin 4B of this group of disazo dyestuffs stands in close relation to the congo-red ; the only difference being the two $CH_3$ groups on the benzidin.  Its blue sols obtained by E D correspond in all their behaviour to the congo-blue sol.

The colloidally dissolved electro-positive " *night blue* " (*Nachtblau*) is in many respects a counterpart to the above discussed disazo dyes. This rosanilin dye has a basic amino group, which is transformed into the ionic imonium group by a quinoid rearrangement.  Here the blue quinoid electropositive form constitutes the ionogenic complex.

By E D the finely dispersed blue sol of the dye salt, for example the chloride, is converted into a stable lilac-red sol with a pronounced

[22] Experiments with F. Lang, *not yet published.*

coarsely dispersed suspensoid character. The neutral part forms therein the red, strongly associated pseudo-base, an imine, which is produced by hydrolysis as a result of E D. On this imine there are attached some isolated polar imonium groups. The *Gegenions* are here either OH ions, which become easily replaced, in air, by $HCO_3$ ions or probably the rest of the original Cl ions which, as with our iron oxide sol, have not been removed by E D. Heating can in general produce only a small increase in conductivity as a result of greater ionic mobility. A greater hydrolysis would, in contrast to congo-blue sol, only increase the neutral part at the cost of the ionogenic complex and therefore decrease the total charge. This relationship can be expressed in a steeper slope of the linear temperature-conductivity curve. It is of especial interest that the reduction of the degree of dispersion of night blue (*Nachtblau*) corresponds with the displacement of the maximum absorption of the long wave-lengths. Therefore the behaviour is opposite to that of congo red. Nevertheless the course of the association and colour displacement is, in both cases, to be consistently understood from a chemico-constitutive point of view.

## Gums.

Finally, very brief mention should be made of certain kinds of gums (*e.g.*, gum arabic and gum tragacanth) because of the behaviour of their ionic complexes. Gum arabic contains, as shown by recent work,[23, 24] a complex compound of a *d*-glycuronic acid with galactose, on which other carbohydrates (*d*-galactose, *l*-arabinose, rhamnose) are connected by means of glycosidial linkages. The *d*-glycuronic acid can be prepared in a relatively good yield from gum arabic by the method of F. Weinmann.[25] The gum-arabic sol is converted by energetic E D into an almost ash-free acidoid sol, in which the complex glycuronic acid can be regarded as the ionogenic complex. The attached carbohydrate together with the non-ionogenic part of the glycuronic acid constitute the neutral part. The conductivity of this highly purified gum sol shows an extremely characteristic course on heating.[26] A maximum is reached at about 70° with increasing temperature, followed by a fall (Fig. 3). However, if the gum sol is neutralised the conductivity-temperature curve approaches a straight line, with a slight tendency to curve upward. This effect with acid sol can with certainty be accredited to the decrease of the dissociation constant of the ionogenic acid with increasing temperature, which finally over-compensates the increase of ionic mobility with higher temperature. On the other hand, pure isolated *d*-glycuronic acid shows no maximum, but only a linear increase of the conductivity in our temperature range up to 95° C. Gum tragacanth shows the same behaviour as a gum-arabic sol. The electrochemical properties of the glycuronic acid in the sol appear to be materially changed by its linkage with the carbohydrate. In any event, we must not forget that the linking of many acid complexes in the colloid particle can lead to important local disturbances in the activity relations. At present we have no deep insight into these things.

In its classical period all the tendencies of colloid chemistry were first directed to ascertaining as well as possible, the features common

[23] C. L. Butler and L. H. Cretcher, *J. Am. Chem. Soc.*, **51**, 1519, 1929.
[24] A. J. Norman, *Bioch. J.*, **23**, 524, 24, 1929.
[25] *Chem. Ber.*, **62**, 1637, 1929.
[26] Pauli and E. Ripper, *Koll. Z.*, **62**, 162, 1933.
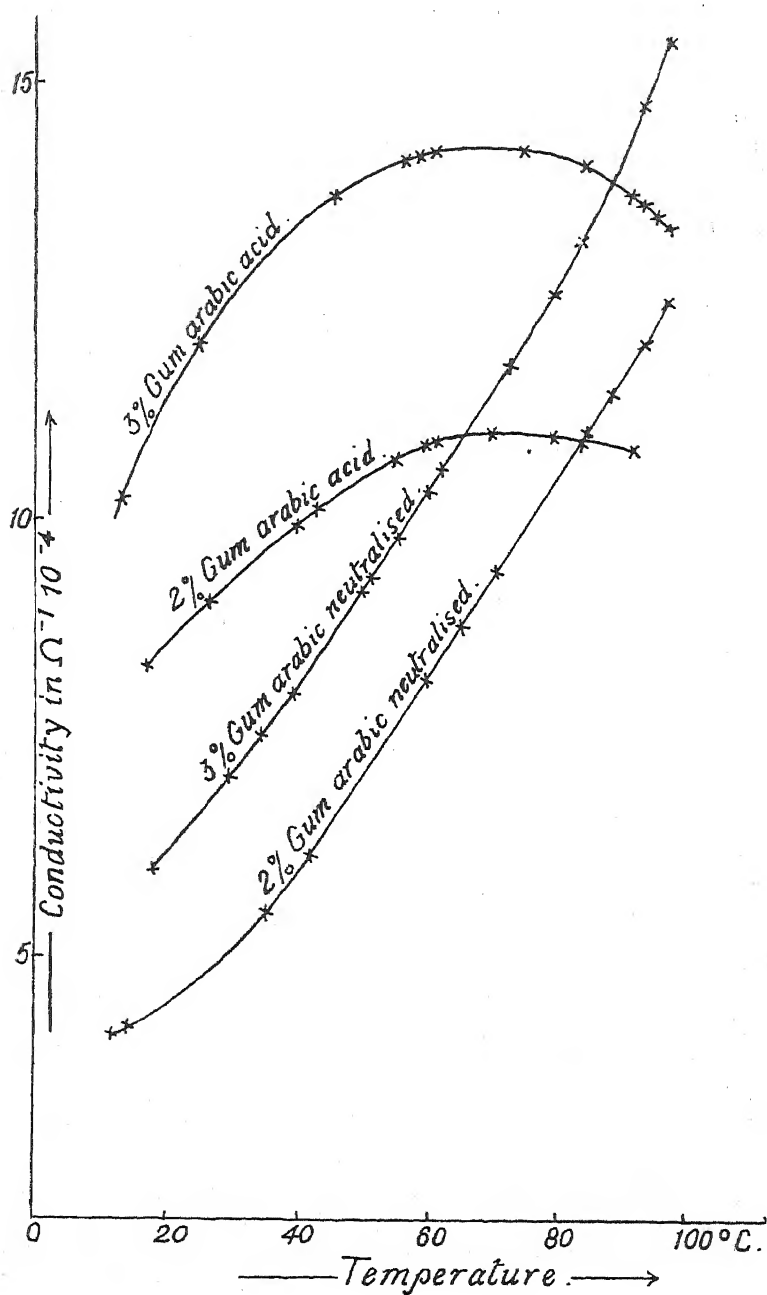
FIG. 3.

to all the phenomena and to formulating the general laws. Thus in the electrochemistry of the colloids we have gradually succeeded in learning its relations to the theories of the strong and especially the polyvalent electrolytes and, on the other hand, in recognising the transitions to the phenomena of the electrical charge of walls and membranes. All the relations and changes between mixed crystal and complex formation are clearly visualised if we can see what happens in the colloid particle
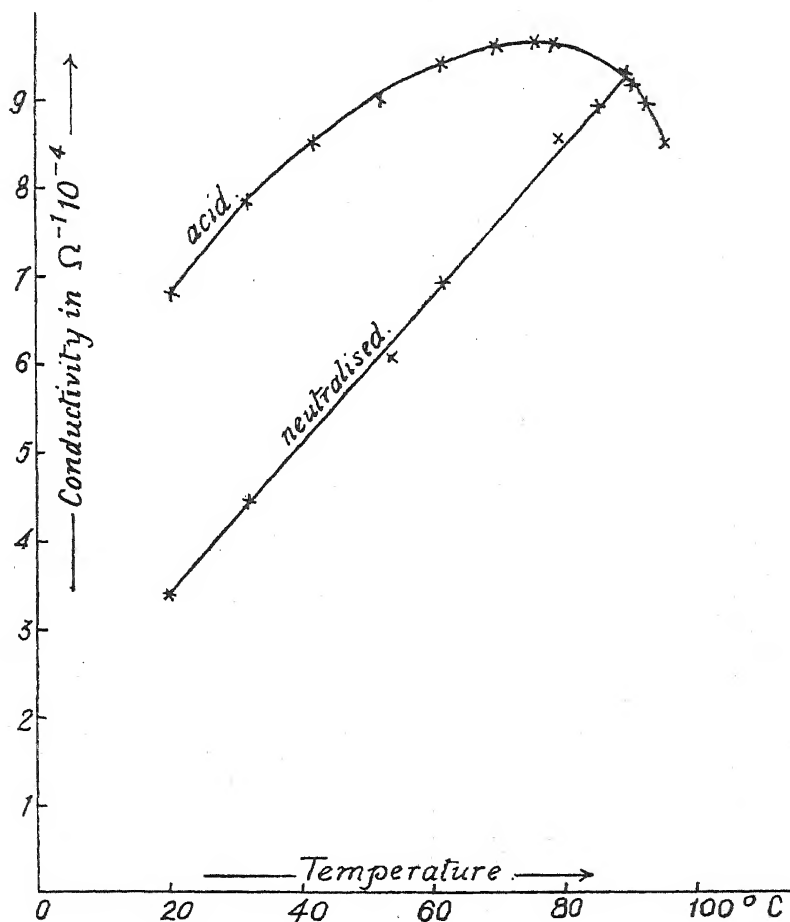


FIG. 4.—1 per cent. gum tragacanth.

from the surface towards the interior. The advance in the preparation of pure colloids leads us finally to the consideration of the isolated building stones ; to the possibility of varying them in a definite manner and of studying the reaction of the constitutional variation on the electrochemical and colloidal behaviour. A classification in this field, which at present could only be illustrated by a few examples, must be reserved for a later time.

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# IONIC MICELLE OR ELECTRIC DOUBLE LAYER.

## By H. R. Kruyt.

The dynamics of colloids are founded on Hardy's investigation [1] of 1900 on the sol of denaturated albumen : when moving electrophetically colloids are *stable*, when not, *unstable*. (In principle, the rule holds even for lyophylic colloids if the stabilisation in consequence of solvatation [2] is taken sufficiently into account.)

Hardy's result is generally interpreted thus : the particles have a tendency to coalesce (free surface energy, van der Waals' attraction), they are inhibited from doing so by electric repulsion, for the electrophoretic movement is a measure for the particle's charge or better for the potential of its double layer.

However, between Hardy's experimental facts and this interpretation lies a series of theoretical considerations. In the first place, electrophoresis is considered to be an electrokinetic process, absolutely adequate to electrosmosis and streaming potentials, the periphery of the particle being strictly comparable to the wall of the capillary tube in the latter processes. Then, the Helmholtz-Gouy theory is thought to be the quantitative interpretation of the phenomena. And, finally, coagulation is understood kinetically in the sense of von Smoluchowski's theory of rapid coagulation. It seems unnecessary to mention here the numerous investigations which have been carried out to elucidate each of these assumptions.

There is, however, another analogue for electrophoresis than electrosmosis and streaming potentials, *viz.*, electrolytic conductivity. In this trend of thought, the particle is considered as a highly polyvalent ion, an ionic micelle ; Hardy's dynamical result then postulates that the colloidal particle is stable in consequence of its ionisation, coagulation being the result of decreased ionisation ; the theory of the kinetics of coagulation is the same with either conception.

In both cases we meet with an extrapolation ; the first theory extrapolates our knowledge of the phenomena at a macro-wall to those on the colloidal ultramicro-wall ; the second theory extrapolates our knowledge of molecular and ionic dispersed systems to those of the ultramicrodispersed systems. One is an extrapolation to smaller, the other to larger dimensions.

Is the first extrapolation allowable ? There can be hardly any doubt about this ; there is only the Debye-Hückel question,[3] whether the coefficient in the potential equation be 4 or 6, but even this seems to be settled.[4] The Helmholtz-Gouy theory is as readily applicable to a small

[1] W. B. Hardy, *Z. physik. Chem.*, **33,** 385, 1900.
[2] H. R. Kruyt and H. G. Bungenberg de Jong, *Z. physik. Chem.*, **100,** 250, 1922, and the series : *Zur Kenntnis der lyophilen Kolloide* in *Kolloidchem. B.* since Vol. **28,** 1928.
[3] P. Debye and E. Hückel, *Physik. Z.*, **25,** 49, 1924.
[4] D. C. Henry, *Proc. Roy. Soc.*, **133A,** 106, 1931.

and spherical wall as to a large and flat one.    Therefore, one can hardly speak of extrapolation in this respect.

With the extrapolation from our knowledge of ions to electrically charged micelles we meet with quite another extrapolation.  Our knowledge of ions is almost limited to that for 1·1, 1·2 and 2·1 electrolytes ;  only when the charges are close to each other does the modern theory give satisfactory results.  With large molecules (complex ions) and with polyvalent ions (3, 4 valent, etc.), unknown ionic radii play an important rôle in any calculation.  The extrapolation from, say, 1·2 electrolyte to, say, a colloidal gold particle is enormous, and the more risky as the intermediate links fail.  One could doubt, however, the quantitative correctness of the Helmholtz-Gouy theory ;  but every doubt in this respect applies as much to the Debye-Hückel theory, which is founded on the same reasoning.

As a morphological description of the surface of the particle, it is absolutely arbitrary, whether we look upon it as a wall with an electric double layer or as a polyvalent electrolyte.   As we want, however, more than such description, as we want quantitative information about the statics and dynamics of colloids, we must prefer a conception which enables us at the time being to account for the behaviour of colloids, so far as this is known by measurements.   In that respect it is nowadays more advantageous to look upon the surface as bearing an electric double layer, analogous to that which gives rise to electrokinetic phenomena, than to consider the whole particle as an electrolyte with high polyvalency and an enormous " ionic " radius, since such a conception does not enable a quantitative interpretation of facts, and cannot elucidate the mechanism of colloid behaviour.

Though we must, therefore, prefer nowadays the classical theory as being the more fruitful one (the only criterion for the value of a theory being its fruitfulness), we should not be blind to its shortcomings.

First of all, the mere statement that an electric double layer is present on a stable micelle is unsatisfactory ;  we immediately meet with two questions :

(a) What is the origin of this double layer ;  and
(b) Does every $\zeta$ potential act as a stabilising factor ?

As to its origin, two main possibilities have been considered :

1. The electrolytes, whose ions build up the double layer, are adsorbed by the wall from the liquid, and if no electrolyte is present, it is the ions of water itself.

2. The material of the wall is ionogenic, the molecules at the periphery contain the ion of the inner coating, the other ion is dissociated into the liquid and builds up the diffuse layer of " counter ions " (gegenions).

Formerly, the first explanation was considered the better ;[5] it is, however, unsatisfactory, as it leaves the question open in most cases, why one ion should be preferably adsorbed.  Recently, the latter reasoning is the more accepted ;[6] it gives a more complete insight and it accounts better for many facts.  Moreover, it is a mean between the two conceptions mentioned in the title of this paper.  However, we should be conscious that neither the question (a) nor (b) is settled in this way.

[5] H. Freundlich, *Kapillarchemie*, 1. Ed. of 1909.
[6] Already since H. Freundlich and G. von Elissafoff, *Z. physik. Chem.*, **79,** 385, 1912.

One should keep in mind that an absolutely non-ionogenic material, such as naphthaline, or even paraffin, shows a very high electro-kinetic potential against pure water,[7] but that, nevertheless, they give no stable colloids.

This suggests that we must discriminate between two sources of $\zeta$-potential. I shall try to elucidate this problem by two examples, one of a hydrophobic material, silver halide, studied in recent years by my pupils, and the other of the hydrophylic material, gum arabic, studied (amongst many other colloids) by Bungenberg de Jong and his pupils.

AgI formed from $AgNO_3$ and KI in strictly stoichiometrical proportions does not give a stable colloid ; for such, a surplus of either KI or $AgNO_3$ is necessary, the former giving a negatively, the latter a positively charged sol.[8]   I-ions increase the negative $\zeta$-potential, that exists already at the surface of AgI against water, Ag-ions decrease it and in larger concentration make it change positively.   This has been investigated for electrophoresis, electrosmosis [9] and streaming potentials.[10] *  The amount of active I-ions in the inner coating ($a$) can be measured in regard to their dependence upon the KI concentration ($c$).   The relation is not that of an adsorption : [11]

$$\text{d} \log a = k_1 \, \text{d} \log c,$$
but
$$\text{d}a = k_2 \, \text{d} \log c,$$

which suggests the partition of an ion, which determines the potential, over two phases, at constant capacity of the double layer.   Moreover, the maximum number of I-ions in the inner coating, never exceeds the number of Ag-ions on the edges of the lattice of the particle.   It is evident that we are dealing not with plane but with linear double layers. To consider such a particle as an ionic micelle would have no value, even if the lattice were an ionic lattice and the double layer a consequence of ionic forces.

Now, the stability of an AgI-sol is governed only by the $\zeta$-potential induced by I-ions and Ag-ions (or ions in " isomorphic " relation with these, $i.e.$, which can be taken up in the lattice [11, 12]).   Other ions can, however, make the $\zeta$-potential increase,[10] but they themselves cannot stabilise a sol, which lacks I-ions in the inner coating.   So, from the colloid standpoint we must discriminate between the $\zeta$-potential caused by " potential-determining " electrolytes and others.

Along quite another line of reasoning de Jong's investigations [13] lead to a similar conclusion.   In his studies on complex coacervation he wanted to know the charge on a gum arabic particle.   He determined [13] what is called equivalent aggregation or the " equivalent weight of the colloid ion," first by analysis of its salts.   He found the value 1210, in accordance with other measurements made by Thomas and Murray.[14]   On the

* Strangely, only very small particles can be charged positively by Ag-ions.[10] This was a first indication that these ions can find place only at the edges and corners of the particles but not at the faces.

[7] J. Perrin, $J. chim. physique$, **2**, 601, 1904 ; P. F. J. A. Julien, $Theses$, Utrecht, 1933.

[8] A. Lottermoser, $J. prakt. Chem.$, **68**, 341, 1903 ; **72**, 39, 1905 ; **73**, 374, 1906.

[9] R. Labes, $Z. physik. Chem.$, **116**, 1, 1925.

[10] P. F. J. A. Julien, $Theses$, Utrecht, 1933.

[11] E. J. W. Verwey, $Theses$, Utrecht, 1934 ; E. J. W. Verwey and H. R. Kruyt, $Z. physik. Chem.$, **167**, 137, 149, 312, 1933-34.

[12] H. R. Kruyt and P. C. van der Willigen, $Z. physik. Chem.$, **139**, 53, 1928 ; H. A. Cysouw, $Theses$, Utrecht, 1934.

[13] A series of twenty papers in $Biochem. Z.$ since 1929.

[14] H. G. Bungenberg de Jong and P. van der Linde, $Biochem. Z.$, **262**, 161, 1933.

other hand, he measured the so-called reciprocal " hexol number," which is a measure for the quantity of a hexavalent ion, bound when the electrokinetic activity is exactly compensated. According to this method, the equivalent weight was 705. This difference is by no means specific for arabine derivates; with a number of other colloids he got similar results. The conclusion is that there are more electric units on a particle than there are ionogenic spots. In other words : in addition to the electric charges due to the ionisation of molecules at the surface of the particle surface there is another source of electrokinetic activity. This second type has always a negative sign, when water is the surrounding liquid ; we thus met with it in the case of paraffin as well as with a hydrophobic crystalline particle such as AgI and, also, with hydrophylic colloids such as gum arabic.

What may be the structure of the double layer in these cases ? I do not venture to give a decisive answer to that question ; we are busy investigating the problem further. I do not think the hydroxyl ions of water can be made responsible for it, for then the influence of H-ions should be specifically strong, which seems not to be the case.[10]

In conclusion, I might state that it is preferable to look on a colloidal micelle as a surface on which an electric double layer is situated, i.e., to interpret its electric behaviour according to the Helmholtz-Gouy theory. As to the constitution of that double layer, there is no doubt that its inner layer is often built up by ions of the material of the particle itself, or at least by ions which belong homogeneously to the particle. However, another architecture is not only possible, but even always present. The former type of double layer is, however, the more important for the stability of a colloid.

# THE APPLICATION OF THE DEBYE-HÜCKEL THEORY TO COLLOIDAL ELECTROLYTES.

By G. S. HARTLEY.

The opinion has frequently been expressed that many of the " anomalies of colloidal electrolytes " may be at least partially explicable in terms of the interionic attraction theory which has in recent years received so great a stimulus from the work of Debye and Hückel—*i.e.* by consideration of the interaction due to Coulomb forces of free ions and micelles at distances which, by comparison with the range of molecular forces, are very great. By the " anomalies of colloidal electrolytes " I do not mean the combination of high conductivity with low osmotic pressure which is the distinguishing characteristic of those electrolytes which are colloidal by virtue of aggregation, such as soaps and other long-chain salts and dyes, but the more subtle anomalies in the case of these substances such as the "Hammarsten effect"[1] and the apparent

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[1] There are two distinct phenomena referred to as " Hammarsten effect " : one is the marked influence of the size of the " *Gegenion* " on the osmotic properties of protein salts. The other is the finding of osmotic pressures lower than " would be expected " from the *Gegenion* activity. As van Rysselberghe[4] points out in this connection, the relationship between activity and osmotic coefficients is an integral one and no direct correspondence is to be expected. See note 5.

disagreement between various data which led Mcbain [2] to postulate the existence of two types of colloidal particles in solutions of soaps, and also such apparent disagreements as that found by Pauli and Ripper [3] between electromotive force and conductivity measurements on gum arabic sols. Pauli explicitly states that his results may be due to some special type of Debye-Hückel effect to be found in very unsymmetrical electrolytes, and van Rysselberghe [4] in a recent paper has applied the simple Debye-Hückel equations to explain the observed osmotic pressures of two typical colloidal electrolytes, postulating the aggregation of ions of one kind only. Van Rysselberghe points out that, from the standpoint of the interionic attraction theory, many of these special effects may be in fact merely more complicated cases of the " anomalies of strong electrolytes." It is the object of this paper to examine in more detail how far " ionic atmosphere " considerations are likely to help towards an understanding of the nature of colloidal electrolyte solutions.

Before going further it would be well to consider what was meant by the phrase " anomalies of strong electrolytes." It was complete disagreement between the experimental results and the predictions of the classical mass-action or Arrhenius theory of dissociation. The values for the degree of dissociation of strong electrolytes as calculated from conductivity and, for example, depression of freezing-points were not in good agreement. But still greater was the disagreement among the results at different concentrations when the mass action law was brought into consideration, and therefore the degree of dissociation calculated from electromotive force or other method of determining directly the activity of the solute was in very bad agreement with the results of either of the other methods. [5]

That these anomalies might be explicable in terms of the Coulomb forces was appreciated by Sutherland, [6] Milner, [7] Herz, [8] Bjerrum [9] and others, but it was the mathematical simplification introduced by Debye and Hückel [10] with their conception of the ionic atmosphere that first permitted a quantitative explanation to be found. Their equation for the equilibrium properties and Onsager's for the mobilities have been quantitatively verified in very dilute solutions by investigations too numerous to mention.

[2] McBain, Laing and Titley, *J. Chem. Soc.*, **115**, 1279, 1919.
[3] Pauli and Ripper, *Koll. Z.*, **62**, 166, 1933.
[4] van Rysselberghe, *J. Physic. Chem.*, **38**, 645, 1934.
[5] The activity coefficient as defined by equation (18) and the osmotic coefficient $g$ defined by osmotic pressure $= RT\left(\dfrac{1}{z_+} + \dfrac{1}{z_-}\right)gc$ are related only by an equation which in dilute solution becomes

$$\frac{\mathrm{d}(gc)}{\mathrm{d}c} = \frac{\mathrm{d}\log{(fc)}}{\mathrm{d}\log c}.$$

They will both measure the degree of dissociation when the classical laws apply, but when their deviations from unity are caused by the interaction of free ions, they will, as measures of the apparent degree of dissociation, not necessarily lead to the same result. Where, as according to the Debye-Hückel theory $f$ has in dilute solution the form $f = 1 - A\sqrt{c}$, $A$ being a constant, it follows that $g = 1 - \dfrac{A}{3}\sqrt{c}$. The osmotic pressure therefore, if calculated from taking $f$ equal to the degree of dissociation will be lower than the observed value.

[6] Sutherland, *Phil. Mag.* (i.a.), **16**, 497, 1908.
[7] Milner, *Phil. Mag.* (i.a.), **35**, 352, 1918.    [8] Herz, *Ann. Physik*, **37**, 1, 1912.
[9] Bjerrum, *Z. Elektrochem.*, **24**, 321, 1918.
[10] Debye and Hückel, *Physik. Z.*, **24**, 185, 1923.

Solutions of colloidal electrolytes, and indeed the majority of hydro-sols contain " ions " (the micelles or colloidal particles) of far higher valence than we are accustomed to dealing with in ordinary electrolytes. Now the deviations from ideality predicted by the theory increase extremely rapidly with increasing valence of the ions, and in view of the fact that large deviations from ideality can be caused by the Coulomb forces between free simple ions, it is clearly unreasonable to assume that these micelles or particles will obey the classical laws. It is well-known however that the simple Debye-Hückel theory badly fails to represent the facts for electrolytes of high valence type in any but the most dilute solutions, and we may therefore find that the deviations *from the theory* will be of equal importance with the deviations *from classical laws* predicted *by* the theory. Consideration of the limitations and extensions of the theory will be an essential feature of its application to colloidal electrolytes.

The conception of an " ionic atmosphere " around colloidal particles is by no means new to colloid science. Gouy[11] produced his theory of the " diffuse double layer " thirteen years before the Debye-Hückel theory was published, and, as Hückel[12] points out, the von Smoluchowski cataphoresis formula is essentially the same thing as the Debye-Hückel-Onsager ionic mobility equation, the two becoming, for very large and high-valent spherical ions, exactly equivalent when a necessary numerical correction to the former has been made. Whether developments along the lines here discussed are to be considered as developments of the Debye-Hückel theory or the theory of the diffuse double layer, is entirely a question of the mental background of the investigators interested.

## The Debye-Hückel Theory.

This theory seeks to explain the anomalies in the equilibrium pro-perties (freezing-point depression, E.M.F. etc., as distinct from conduc-tivity, viscosity, etc.) of dilute solutions of strong electrolytes in terms of the influence of the incomplete randomness of the distribution of the ions on their potentials—*i.e.* on the work necessary to discharge them by a hypothetical reversible process. The phrase " incomplete randomness of distribution " is used here in preference to " atmosphere " in order to emphasise that under the conditions in which the theory is quan-titatively applicable the atmospheres have no sort of individuality. They are mutually interwoven and the average concentrations of ions in them are nowhere greatly different from those in the solution as a whole.

The effect of the distribution on the potentials of the ions must first be determined. This was effected by Debye and Hückel by means of a combination of the Poisson and Boltzmann equations. I prefer, for reasons which will appear later, to present the derivation in a slightly different, though exactly equivalent, way.

A force $P$ per gm. mol. acting on the molecules of an ideal solute in dilute solution will produce a concentration gradient $dc/dx$, the force being considered to act parallel to the $x$-axis. Equating the free energy increase on transferring an infinitesimal quantity of the solute from

[11] Gouy, *J. Physique*, (4), **9**, 457, 1910.
[12] Hückel, *Physik. Z.*, **25**, 204, 1924.

a concentration $c$ to one $c + dc$ with the work done against the force for a distance $dr$, we obtain, as the condition of equilibrium,

$$- RT\mathrm{d} \log c = - P \cdot \mathrm{d}r \quad . \quad . \quad . \quad . \quad (1)$$

or

$$\frac{\mathrm{d} \log c}{\mathrm{d}r} = \frac{P}{RT} \quad . \quad . \quad . \quad . \quad (2)$$

Now if we are dealing with ions in a gradient of electrical potential $\frac{\mathrm{d}\psi}{\mathrm{d}x}$, the force on each ion will be $- z_i\epsilon\frac{\mathrm{d}\psi}{\mathrm{d}x}$ where $z_i$ is the algebraic valence of the ion considered. If the concentrations of the ions are sufficiently small, we may assume that the gradient of concentration for the ions will be governed by the same equation (2) as that of the molecules subjected to a mechanical force, whence we obtain, bearing in mind that the force $P$ acts on $N$ molecules where $N$ is the Avagadro number,

$$\frac{\mathrm{d} \log c_i}{\mathrm{d}x} = - \frac{z_i\epsilon}{kT} \cdot \frac{\mathrm{d}\psi}{\mathrm{d}x} \quad . \quad . \quad . \quad (3)$$

where $k = R/N$ is the Boltzmann constant. By integration of (3) we obtain

$$c_i = \bar{c}_i \cdot e^{-z_i\epsilon\psi/kT} \quad . \quad . \quad . \quad (4)$$

where $\bar{c}_i$ is the concentration of the ions $i$ at zero potential. Equation (4) is the Boltzmann equation. The units in which concentration is measured are of no importance for the validity of these equations, and we shall find it most convenient to measure it in gm. *equivalents* per c.c., but *reckoned negative for negative ions*.

Now if we are dealing with distribution round a spherical ion and this distribution, which on an average it must be, is spherically symmetrical, we may apply equation (3), substituting the radius $r$ for $x$. If, inside a spherical shell of radius $r$, the total valence of the central ion *plus* that part of the atmosphere inside $r$ is $\bar{z}$, the force per unit charge outwards at $r$, *i.e.* the gradient of potential, will be

$$\frac{\mathrm{d}\psi}{\mathrm{d}r} = \frac{\bar{z}\epsilon}{D \cdot r^2} \quad . \quad . \quad . \quad . \quad (5)$$

since a spherically symmetrically distributed charge acts on charges outside it as if the whole charge were concentrated at the centre, and any spherically symmetrically distributed charge *outside* the radius $r$ will produce no force on ions *inside* it. Combining equations (3) and (5) we obtain

$$\frac{\mathrm{d} \log c_i}{\mathrm{d}r} = - \frac{\epsilon^2}{DkT} \cdot \frac{z_i\bar{z}}{r^2} \quad . \quad . \quad . \quad (6)$$

A spherical shell of radius $r$ and thickness $dr$ will contain a slight excess of ions of one kind of charge over those of the other, and the resulting valence of the shell will be

$$\mathrm{d}\bar{z} = 4\pi r^2 \cdot \mathrm{d}r \cdot N \cdot \Sigma c_i \quad . \quad . \quad . \quad (7)$$

Differentiating (5) with respect to $r$ and substituting (7) we obtain

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\psi}{\mathrm{d}r}\right) = - \frac{4\pi N \epsilon}{D}r^2 \Sigma c_i \quad . \quad . \quad . \quad (8)$$

Substituting equations (3) and (4) we have

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\psi}{\mathrm{d}r}\right) = \frac{4\pi N \epsilon}{D}r^2 \Sigma c_i \cdot e^{-z_i\epsilon\psi/kT} \quad . \quad . \quad (9)$$

In the case where all the $z_i \epsilon \psi / kT$ values can be considered $\ll 1$, this equation may be written

$$\frac{d}{dr}\left(r^2 \frac{d\psi}{dr}\right) = \frac{4\pi N \epsilon^2}{DkT} \cdot r^2 \cdot \sum \bar{c}_i \cdot z_i \quad . \quad . \quad . \quad (10)$$

which permits of a simple solution, namely

$$\psi = A \cdot \frac{e^{-\kappa r}}{r} + B \cdot \frac{e^{+\kappa r}}{r} \quad . \quad . \quad . \quad (11)$$

where

$$\kappa^2 = \frac{4\pi N \epsilon^2}{DkT} \cdot \sum \bar{c}_i z_i \quad . \quad . \quad . \quad (12)$$

Since the potential $\psi$ must be zero for large values of $r$, if the $\bar{c}_i$'s are the bulk concentration. the constant $B$ must be zero. The constant $A$ is obtained from the limiting form of equation (5), where $r$ is put equal to $a$, the distance of closest possible approach of two ions (considered to be the same for all ions concerned) in which case $\bar{z}$ is simply the valence $z_k$ of the central ion. Making these substitutions equation (11) becomes

$$\psi_{k,\,r} = \frac{z_k \cdot \epsilon}{D} \cdot \frac{e^{\kappa a}}{1 + \kappa a} \cdot \frac{e^{-\kappa r}}{r} \quad . \quad . \quad (13)$$

the well-known solution of Debye and Hückel. The potential $\psi_{k,\,a}$ at the surface of the ions is given by

$$\psi_{k,\,a} = \frac{z_k \cdot \epsilon}{Da} \cdot \frac{1}{1 + \kappa a} \quad . \quad . \quad . \quad (14)$$

The simplest method of passing from the equation for the potential of the ion to the measurable properties of the solution is to consider the work necessary to discharge a very small fraction of the ions, thus leaving the value of $\kappa$ unchanged, so that the potential of the ions being discharged is always directly proportional to their residual charge. This work is therefore equal to

$$-\frac{z_k^2 \epsilon^2}{2Da} \cdot \frac{1}{1 + \kappa a} \quad . \quad . \quad . \quad (15)$$

The work of discharging 1 gm. equivalent of an electrolyte whose ions have numerical valences $z_+$ and $z_-$ in an infinite volume of solution will therefore be

$$- N \cdot (z_+ + z_-) \cdot \frac{\epsilon^2}{2Da} \cdot \frac{1}{1 + \kappa a} \quad . \quad . \quad (16)$$

The work done therefore in discharging the electrolyte in a solution I and recharging it in a solution II will be

$$- N(z_+ + z_-) \cdot \frac{\epsilon^2}{2Da} \cdot \left[\frac{1}{1 + \kappa_1 a} - \frac{1}{1 + \kappa_{II} a}\right] \quad . \quad . \quad (17)$$

Now the increase of free energy on transferring 1 gm. equivalent of this electrolyte from solution I to solution II will be

$$- RT\left[\frac{1}{z_+} \log \frac{c_{+,\,II}}{c_{+,\,I}} + \frac{1}{z_-} \log \frac{c_{-,\,II}}{c_{-,\,I}}\right] - \left(\frac{1}{z_+} + \frac{1}{z_-}\right) RT \log \frac{f_{II}}{f_I} \quad . \quad (18)$$

where the term in square brackets would be the increase of free energy if the ions behaved as molecules of an ideal solute, $c_+$ and $c_-$ with appropriate suffixes being the concentrations of the two kinds of ions in the two solutions. The second term serves to define the mean activity coefficients $f$. Now the Debye-Hückel theory postulates that the ions

would behave as molecules of an ideal solute if their charge were removed, and the second term is therefore the additional work rendered necessary by virtue of the electric charge, *i.e.* the quantity (17), whence

$$- RT \log \frac{f_{\mathrm{II}}}{f_{\mathrm{I}}} = - N \cdot z_+ z_- \cdot \frac{\epsilon^2}{2Da} \cdot \left( \frac{1}{1 + \kappa_{\mathrm{I}} a} - \frac{1}{1 + \kappa_{\mathrm{II}} a} \right) \qquad (19)$$

Now if solution II is simply an infinitely dilute solution, $\kappa_{\mathrm{II}} = 0$ and $f_{\mathrm{II}} = 1$, whence, omitting the remaining suffix,

$$RT \log f = z_+ z_- \frac{N\epsilon^2}{2Da} \left( \frac{1}{1 + \kappa a} - 1 \right) \qquad . \qquad . \quad (20)$$

or
$$- \log f = z_+ z_- \cdot \frac{\epsilon^2}{2DkT} \cdot \frac{\kappa}{1 + \kappa a} \qquad . \qquad . \quad (21)$$

from which it appears that when $\kappa a \ll 1$, $\log f$ is proportional to $\kappa$, which in turn (equation (12)) is proportional to $\sqrt{\Sigma c_i z_i}$, *i.e.* to the square root of the ionic strength $\left( = \frac{\Sigma c_i \cdot z_i}{2} \right)$. It is further proportional to the product of the valences of the ions. These predictions have frequently been verified for dilute solutions of electrolytes of low valence type.

Discussion of the atmosphere effects on the mobilities of ions may be conveniently deferred to a later section. We shall next consider some of the limitations of the theory.

### Limitations and Extensions of the Theory.

The assumption was made in writing the general equation (9) in the simplified form (10) which enables an explicit solution to be found, that all the values of $z_i \epsilon \psi / kT$ are $\ll 1$. Since $\psi_{k, r}$ is approximately equal to $z_k \epsilon / Dr$ for small values of $r$, we may write

$$\frac{z_i \epsilon \psi}{kT} \simeq \frac{z_i z_k \epsilon^2}{DkT \cdot r} \qquad . \qquad . \qquad . \quad (22)$$

since $\epsilon^2 / DkT$ for water at 25° C. $= 7\cdot08 \times 10^{-8}$ cm., we see that $r$ must be as great as $7\cdot08$ Å. before the value of $z_i \epsilon \psi / kT$ is less even than 1 even for a uniunivalent electrolyte. The quantitative success of a theory based on an assumption apparently so invalid is explained by the following considerations.

In the upper portion of Fig. 1 are plotted the values of

$$\frac{\bar{z}}{z_k}, \ (1) \ ; \quad \frac{1}{z_k} \cdot \frac{\mathrm{d}\bar{z}}{\mathrm{d}(\kappa r)}, \ (2) \ ; \quad \frac{1}{z_k} \cdot \frac{1}{\kappa r} \cdot \frac{\mathrm{d}\bar{z}}{\mathrm{d}(\kappa r)}, \ (3),$$

as functions of distance from the central ion in units of $1/\kappa$ (*i.e.* as functions of $\kappa r$). The total area under curves (2) and (3) is unity. The area under curve (2) between any two ordinates, represents the fraction of the charge of the whole atmosphere which resides between the corresponding radii. The corresponding area under curve (3) represents the fraction of the additional potential of the central ion due to the atmosphere which is contributed by that part of the atmosphere which resides between these radii. Using $1/\kappa$ as the unit of length has the advantage of making these curves of general validity as long as the Debye-Hückel approximation can be considered to hold. The representation is easily extended to finite values of $a$ by eliminating the portions of the curves to the left of $\kappa a$. New unit ordinates for the

curves must be taken. For the first two, the unit will be the original value of $\bar{z}/z_k$ at $\kappa a$ [13] : if this is also taken as the new unit ordinate for the third curve, the areas below it will represent the contributions to potential expressed as fractions of the total potential due to the atmosphere for $a = 0$, but if we wish these areas to measure the contributions as fractions of the total potential due to the atmosphere *for the value of " a " concerned*, we must change our unit further by dividing it by $(1 + \kappa a)$.

Now the value of $1/\kappa$ for a $N/10,000$ aqueous solution of a uniunivalent electrolyte is about 300 Å. The value of $r$ for which $e\psi/kT$ will be equal to $1/10$ is about 60 Å., so that in this case the Debye-Hückel approximation must hold reasonably well for all values of $\kappa r$ above about 0·2 (dotted ordinate marked 1 . 1 . $10^{-4}$). It will be seen that only a very small fraction of the atmosphere is to be found within this radius and therefore considerable error in equation (13) for smaller radii will not make any serious difference to the effective valence $\bar{z}$ within this radius and will therefore not seriously affect the validity of equation (13) for higher values of $r$. Over 80 per cent. of the contribution to the potential made by the atmosphere is made therefore by the part of it to which the equation *can* be expected to apply. At lower concentrations the limiting value of $\kappa r$ will be lower, and the approximation still better, while for higher concentrations and higher valence types it will become pro-



FIG. 1.

gressively worse : this is illustrated by consideration of the other dotted ordinates representing the limiting radius, on the same arbitrary standard (no value of $z_i e\psi/kT$ to exceed $1/10$ outside this radius) for different solutions, 1 . 1 . $10^{-2}$ referring to uniunivalent electrolyte at $N/100$ and 1 . 4 . $10^{-3}$ referring to unitetravalent electrolyte at $N/1000$. Below these curves are given, with the same abscissæ, the concentrations of the two ions around a central ion taking the average concentration in the solution as a whole as unit. Curves are given for the two
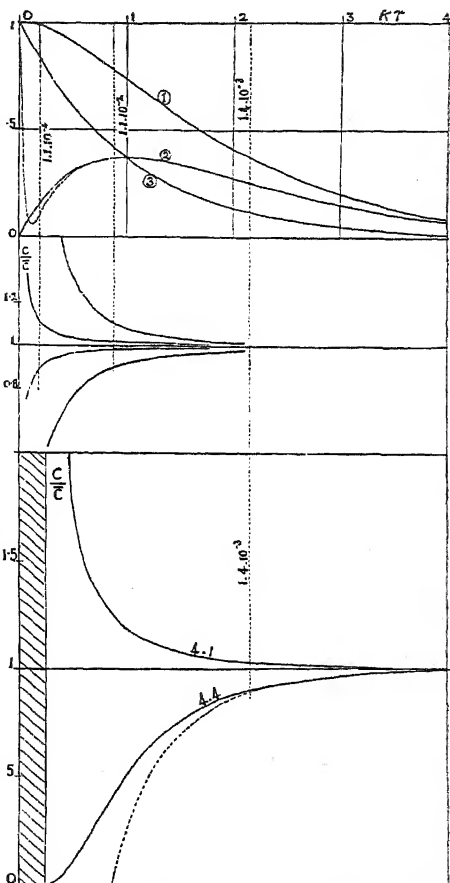
[13] This method of representing the distribution of the atmosphere is due to Scatchard, *Chem. Reviews*, **13**, 10, 1933.

concentrations of uniunivalent electrolyte and for the unitetravalent electrolyte, the distribution in the latter case being about the tetravalent ion. These relative concentrations are more nearly the same function of the radius than of $\kappa r$ and they are consequently displaced along the $\kappa r$ scale on changing the concentration. With increasing concentration a greater fraction of the atmosphere is contained in the region to which the Debye-Hückel approximation cannot apply and we therefore expect to find an increasing deviation from equation (21) as the concentration is increased.

Extensions of the theory in an effort to overcome the limitations have been made chiefly in two ways. The problem of the complete solution of the fundamental differential equation (9) has been attempted, and a theory of ion association, which treats separately the parts of the atmosphere where $z_i e\psi/kT$ is great, has been developed. The latter is due to Bjerrum.[14] The complete solution has been effected by Gronwall and collaborators [15] by an analytical method which involves a very elaborate mathematical treatment, and, since a high degree of accuracy is hardly worth attempting in the solution of an equation whose physical basis is not completely sound, the simple graphical method of Müller [16] seems therefore preferable. These authors find that, with small ions, the deviation from equation (21) as we proceed up the concentration scale, first occurs in the sense of making $f$ smaller than this equation predicts (greater deviations from ideality). For very high values of $a$, conformity with equation (21) must be reached. For intermediate values of $a$ in the case of unsymmetrical electrolytes, deviation first occurs, according to the author's own calculations, in the opposite direction (smaller deviation from ideality). At high concentrations the deviation is always in the latter sense.

We will endeavour to find a qualitative explanation of these tendencies. If the third curve in the upper part of Fig. I is reconstructed on the basis of the curves in the lower part (which will themselves not be in very great error for low values of $r$, as the atmosphere terms in equation (13) are there small) its course for very low values of $r$ is found to be radically altered : a sharp minimum is found for $r \simeq 3 \cdot 5 \, z_+ \cdot z_- \, \text{Å}$. The dotted curve is an approximate one for uniunivalent salt at $N/100$. At extremely low concentrations the fraction of the atmosphere contained within the radius at which this minimum occurs will be negligibly small, but as the concentration is increased it will become greater and will therefore cause more of the atmosphere to be situated near the central ion, where its effect on the potential is very great, than the Debye-Hückel approximation allows. Bjerrum treats this part of the atmosphere separately : he works out the probability of an oppositely charged ion being found within this radius and this combination he considers as an ion-pair—thus redefining the idea of incomplete dissociation in a manner more acceptable to the electron theory of valence : such an ion-pair need suffer no deformation of electron orbits ; the units are temporarily associated purely by electrostatic forces. The volume round an ion within this radius is so small that it seems very unsatisfactory to speak of an average concentration in it ; some such treatment as that of Bjerrum's is an obvious necessity : it is particularly important in dealing with colloidal electrolytes and will be referred to again later.

[14] Bjerrum, *Ergeb. exakt. Naturwiss.*, **6,** 125, 1926.
[15] Gronwall, LaMer and Sandved, *Physik. Z.*, **29,** 358, 1928 ; LaMer, Gronwall and Grieff, *J. Physic. Chem.*, **35,** 2245, 1931.
[16] Müller, *Physik. Z.*, **28,** 324, 1927.

The results of Bjerrum's method and the complete solution method are not markedly different. The increasing importance with increasing concentration of the volume wherein the fraction of the atmosphere is so enormously much greater than is compatible with the Debye-Hückel approximation, explains why the activity coefficient for very small ions should deviate below the Debye-Hückel value; and as the concentration further increases, this volume will contain so much of the atmosphere that the distribution outside it is seriously disturbed and we tend to get deviations in the opposite direction. That deviations in the opposite direction ($f$ greater than would be expected from equation (21), should occur with intermediate ion sizes is best made clear by consideration of the ion concentration-radius curves for an unsymmetrical case where this tendency is most marked. If the $a$ value—the distance of closest approach of the centres of ions—is great enough to block out the volume in which this anomalously large amount of the atmosphere charge might be found, the cause of the first type of deviation will disappear, but another is still left. In the lowest graph of Fig. 1 this portion is shaded out and it will be noticed that there is a considerable gap before we come to the radius (dotted ordinate), beyond which, according to our arbitrary standard, the Debye-Hückel approximation can be considered valid. Now this standard (no value of $z_i \epsilon \psi / kT$ greater than $1/10$) may seem unnecessarily severe in the case of unsymmetrical electrolytes because we can descend to considerably lower radii before the the power of $e$ in the equation for the distribution of univalent ions about tetravalent and of either ion about univalent becomes greater than $1/10$. It must be realised however that the tetravalent ion contributes $4/5$ of the total deviation of $f$ from unity and that the *emigration* of tetravalent ions should produce, according to the Debye-Hückel approximation, $4/5$ of the charge of the atmosphere of the tetravalent ions, the *immigration* of univalent ions producing the remaining $1/5$. Now this will be true of the outer regions of the atmosphere, but it cannot be true when the concentrations of the ions differ considerably from their bulk value simply because the concentration of tetravalent ion *cannot be reduced below zero* but that of the univalent ion can obviously be *increased above* $5/4$ and may reach very high values (it would reach a value of about 7 at the limit of the shaded area) : the dotted curve shows what the concentration of the tetravalent ion would have to be to make its contribution four times that of the univalent ion. In the intermediate region between the shaded area and the dotted ordinate the tetravalent ion is unable to make sufficient contribution to the charge of the atmosphere : on this account the activity coefficient will tend to increase above the Debye-Hückel value : for still lower values of the radius, the much increased concentration of the univalent ions will tend as before to cause the opposite deviation. It is to be expected therefore that the first deviation for very small radii should be in the sense of a smaller $f$ and for intermediate radii in the direction of a larger $f$, and for larger radii still the deviation will diminish and the Debye-Hückel approximation be more closely approached.

## The Breakdown of the Ionic Strength Principle.

According to the simple Debye-Hückel theory, the quantity $\kappa$ equation (12)) is proportional to $\sqrt{\Sigma c_i z_i}$, *i.e.* to the square root of the " ionic strength "; $\log f$ is therefore (equation (21)) also proportional

to the square root of the ionic strength.   This quantity generalises most conveniently the activity-coefficient-determining-power of a solution of an electrolyte or arbitrary mixture of electrolytes, but it is important to notice that it can no longer be of use in considering the deviations from the simple theory.   As soon as we begin to take into consideration higher powers of the exponential in equation (9), quantities in addition to $\kappa$, which are more specialised functions of the valences and concentrations, are bound to occur.   This point also is best made clear by reference to the graph of the concentration about a tetravalent ion, which we will redraw (Fig. 2), with additional curves for the concentrations of tetravalent and univalent ions in another solution when the signs of the ions are reversed but the concentration is the same (*i.e.* curves for a tetravalent *anion* and univalent *cation* about a tetravalent *cation*).   This latter solution will have the same ionic strength as the former, and should therefore form an atmosphere similarly distributed. It is evident that while this will be true in extremely dilute solutions when the outer regions of the atmosphere carry most of its charge, it cannot be true in more concentrated solution where the inner regions become more important.   The charge in any portion of the atmosphere is proportional to the difference of the equivalent concentrations, and when the difference is small it will be the same for the two cases. It increases, however, very much more rapidly for the latter solution than for the former, and as the total charge of the atmosphere must be the same in both cases, it follows that the atmosphere is closer and more effective for the
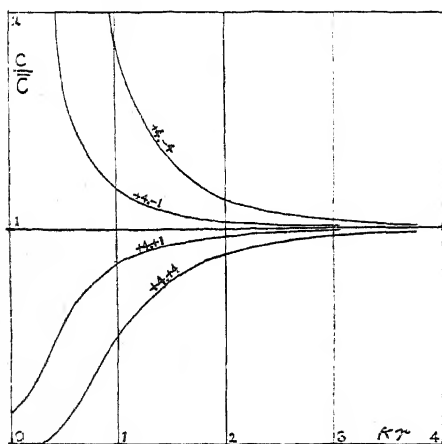


FIG. 2.

latter solution.   In other words, a unitetravalent electrolyte present in large excess of a tetraunivalent one will have a lower activity coefficient than it will when present alone at the same total concentration and *the same ionic strength*.   The more unsymmetrical the electrolyte the more marked will this effect be, and we should finally expect that very high valent micelles will be almost indifferent to the valence of ions of like sign but extremely sensitive to that of those of opposite sign.   The ionic strength principle will give place to an extreme form of Brönsted's specific interaction principle.   One may remark in passing on the obvious relationship of this to the Schulz-Hardy rule.[17]

## The Radius of the Ion and the Thickness of its Atmosphere.

Breakdown of the ionic strength principle undermines the usefulness of the function $\kappa$.   The reciprocal of this quantity is frequently called

[17] For a very interesting theory of the coagulation of colloids, in which the reduction of $\zeta$-potential on the addition of electrolytes is considered as an effect of the atmosphere distribution, see the paper of Müller, *Kol. Beiheft.*, **26**, 257, 1928.

the " radius of the ionic atmosphere," since the charge of the atmosphere would have the same effect on the potential of the central ion if it were situated *entirely* at the distance $1/\kappa$. In cases where the ionic strength principle has ceased to be approximately applicable we can no longer give this physical significance to the quantity defined by equation (12).

It may be emphasised here that the departure from the ionic strength principle in higher concentrations of high valence types will be *reduced* by increasing the radius of the ions *if the " a " values for the various pairs of ions are the same*, and for ions of sufficiently great radius the principle will still be applicable. In such cases, *which will be met with only where we are dealing with a solution containing a large excess of simple electrolytes, so that practically all the ions may approach to within nearly the same distance of the micelle*, $\kappa$ will again have its simple physical significance, but $1/\kappa$ should be called the *thickness* and not the *radius* of the atmosphere. According to equation (14) the potential of the central ion is $\frac{z_k\epsilon}{Da} \cdot \frac{1}{1+\kappa a}$ where $z_k$ is its valence : subtracting the potential $\frac{z_k\epsilon}{Da}$ contributed by the ion itself, we are left with a quantity $-\frac{z_k\epsilon}{D} \frac{\kappa}{1+\kappa a}$ contributed by the atmosphere : this is the value it would have if the whole charge of the atmosphere were situated at a distance $\frac{1 + \kappa a}{\kappa} = a + \frac{1}{\kappa}$ away from the centre of the ion, and therefore a distance $1/\kappa$ from its *surface*. It is important to bear this distinction in mind in order to avoid the mistake of assuming that the theory is invalid in cases where $a$ is greater than $1/\kappa$ on the grounds that an atmosphere " smaller than the ion " is absurd : there is not necessarily any objection to the *thickness* of the atmosphere being less, or even considerably less than the radius of the ion. Those who use the term " diffuse double layer " will not be tempted to make this mistake : the thickness of the diffuse double layer of even a plane charged surface will be the quantity $1/\kappa$ as given by equation (12) provided the $\frac{z_i\epsilon\psi}{kT}$'s are all small.

## The Inconsistencies of the Boltzmann Equation.

In commenting on the slight disagreement between the calculations of Müller (using the simple Güntelberg discharging process which I have used here) and of Gronwall and collaborators (who used the more complicated discharging process of Debye), Onsager [18] draws attention particularly clearly to a fundamental inconsistency in the Boltzmann equation. I have so far attempted to consider only the *mathematical* limitations and extensions of the Debye-Hückel theory, but this inconsistency makes it impossible to avoid introducing a consideration of some of the *physical* assumptions at this stage. Onsager points out that the potential at a distance $r$ from the centre of a $z_k$ valent ion must be related to that at an equal distance from a $z_j$ valent ion by the equation

$$z_j \cdot \psi_{k, r} = z_k \cdot \psi_{j, r} \qquad . \qquad . \qquad . \qquad . \qquad (23)$$

since each of these quantities represents the work necessary to separate

[18] Onsager, *Chem. Reviews*, **13**, 73, 1933.

two such ions from a distance $r$ apart to infinity.   Now the concentration of $j$ ions around a $k$ ion is given by

$$c_j = \bar{c_j} \cdot e^{\dfrac{-z_j \epsilon \psi_{k,\,r}}{kT}} \qquad . \qquad . \qquad . \qquad . \quad (24)$$

and that of a $k$ ion round a $j$ ion by

$$c_k = \bar{c_k} \cdot e^{\dfrac{-z_k \epsilon \psi_{j,\,r}}{kT}} \qquad . \qquad . \qquad . \qquad . \quad (25)$$

It follows directly from these three equations that the two concentration-radius curves should have exactly the same form.

In order to see where the difficulty arises we will draw once again (Fig. 3) the curves for the distribution of the uni- and tetravalent ions about a tetravalent ion in a $N/1000$ solution of a unitetravalent electrolyte.  According to equations (23), (24) and (25) the upper curve (for univalent about tetravalent) should be the same as for tetravalent ions about a univalent one.   The curve for univalent ions about univalent should then be the third curve (for which the logarithms of the ordinates are $-\frac{1}{4}$ times those for the upper curve). Since the upper curves are the same for both ions, the amount of charge contributed to the atmosphere by the *imigration* of ions of *opposite* sign is the same for both ions.   A further amount is contributed by the *emigration* of ions of *like* charge.   Now any shell of the atmosphere (for example that whose radius is represented by the abscissa of $PQ$) will contribute an amount proportional to $PQ$ to the charge of the atmosphere of the tetravalent ion
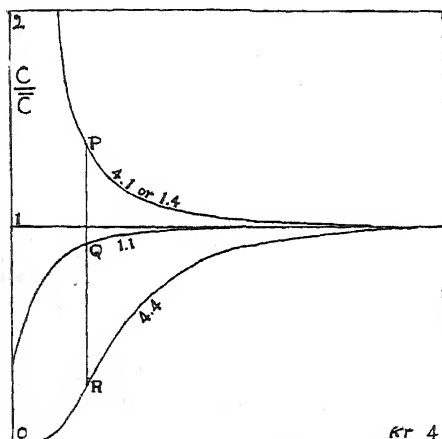


Fig. 3.

and an amount proportional to $PR$ to the charge of the atmosphere of the univalent ion.   Now while it is true that $PR = 4 \cdot PQ$ for sufficiently large values of $r$ it is at once obvious from the figure that in the region where the concentrations diverge at all considerably from the bulk concentration, $PR$ is always less than $4PQ$ (this is quite rigidly true since $\dfrac{e^x - e^{-x/4}}{e^x - e^{-4x}}$ is greater than $\frac{1}{4}$ for all positive values of $x$).

It follows that, no matter by what integration process these curves are obtained, they cannot wholly represent the truth, since they predict that, in any but the most dilute solutions, the charge of the atmosphere of the univalent ions will be greater than $\frac{1}{4}$ times that of the tetravalent. This is clearly absurd, and the Boltzmann equation therefore inapplicable.

The cause of the failure of the Boltzmann equation will be seen if we refer back to its derivation from equation (2).   Equation (2) is only valid so long as the solution can be considered ideal.   We consider the distribution of the ionic atmosphere in order to determine a "macroscopic" activity coefficient, and while doing so we assume that the deviation from ideality does not disturb this distribution itself.   This is a

contradiction. In solutions sufficiently concentrated to make necessary the consideration of the second order terms in equation (9) some type "of microscopic" activity coefficient should be introduced into the derivation of the Boltzmann equation from equation (2), since the ions find themselves in solutions of different local concentrations in different parts of the atmosphere. A further difficulty arises in that we are considering that it is permissible to work with an average concentration at each point of the atmosphere. In dealing with very small volumes this is obviously unsatisfactory. Actually the " concentrations " will be fluctuating widely, and in assessing the values of various properties that the atmosphere possesses by virtue of its charge we may not always be dealing with the same type of average.

### The Preferential Consideration of the Colloidal Ion.

The failure of the Boltzmann equation may seem an unpromising starting-point for an extension of the theory to complicated cases, but certain considerations enable us to proceed with a not too great lack of confidence. In the case of an electrolyte of very unsymmetrical valence type the atmosphere of the multivalent ion has a more obvious physical reality [19] than the atmosphere about the ions of low valence, and the following considerations will show that this natural preference is strengthened by closer inspection. The charge of the near portions of the atmosphere will be due mainly to the increased, and greatly increased, concentration of ions of low valence, the ions of high valence being almost completely absent, and the inner portions of the atmosphere will therefore be quite reasonably symmetrical. In Fig. 4 are shown the concentrations of uni- and 20-valent ions about a 20-valent ion of radius 20 Å., calculated by Müller's method for a concentration of uni-20-valent electrolyte of $N/1000$; it will be seen that within a radius of about 70 Å. the probability of finding another 20-valent ion is extremely small. Only in the outer regions where the volumes are large and the potential effect in any case small will temporary asymmetry due to approach of multi-valent ions be frequent. Further the application of the Boltzmann equation, without some sort of " microscopic activity coefficient " correction to the distribution of univalent ions about a multivalent ion is more defensible than the reverse, since these activity
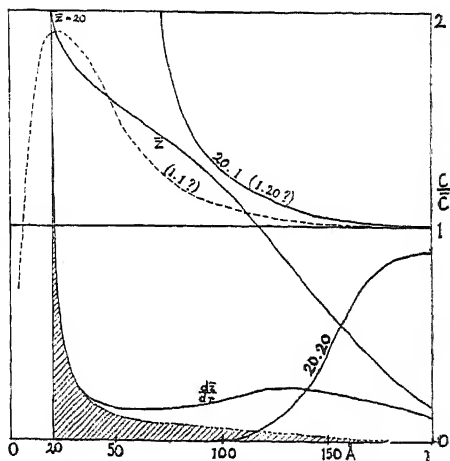


FIG. 4.

[19] One should not, however, regard the atmospheres of micelles as having an exclusive individuality. For the 1-20 valent electrolyte considered, in $N/1000$ solution only about five of the univalent ions will be contained within spheres around the micelles which do not appreciably overlap.

coefficients are not likely to differ very greatly from unity. We shall therefore assume that, in calculating the distribution about the multivalent ions according to the Boltzmann equation and then considering the reverse distribution in the light of this, we shall not be obtaining a very inexact result.

### The Atmospheres of the Gegenions and their Potentials.

Examination of Fig. 4 will show that about one-third of the charge of the atmosphere is contributed by the *immigration of the univalent ions* (in very complete disagreement with the ionic strength principle). The shaded portion of the area under $d\bar{z}/dr$ represents this contribution. If the distribution of multivalent ions about univalent up to the distance of closest approach $a$ is considered to follow the upper curve of the figure in accordance with equations (23), (24) and (25), we must conclude that this atmosphere outside the radius $a$ contains already several times the charge of the central ion if the distribution of univalent is derived in the ordinary way : this difficulty must be partially resolved by giving the distribution of univalent ions some such form as the dotted curve, *i.e.* assuming that the average concentration of univalent ions near any chosen one is *greater* than the bulk concentration : the centres of univalent ions will also usually be able to approach *much closer than a.* The physical picture of this distribution will be somewhat as follows. Any chosen univalent ion is very likely to be found in very close proximity to a multivalent ion, and when so found it is an increased local concentration of its fellows. The univalent ions flock *together* because they flock *around the multivalent ions.*

How are we to compute the work of discharge of the univalent ions ? The potential at the distance $a$ from them will be, according to (23), $1/z$ of the potential at a distance $a$ from the centre of the $z$-valent ion. The potential contributed by the part of their atmospheres *outside the radius a* will therefore be $1/z$ of that for the $z$-valent ion. In the remaining part of the atmospheres the potential can only be reduced, as only the centres of univalent ions are present in this region. The atmosphere contribution to the potentials of the univalent ions must therefore be less than $1/z$ of that for the $z$-valent ions, and will remain so during at least the most important part of the discharging process, so that the contributions of the univalent ions to log $f$ will be smaller than $1/z$ of that of the multivalent. We may, therefore, as a first approximation, neglect the atmospheres of the univalent ions altogether in calculating $f$.

### The Atmosphere Effect on the Mobility of the Multivalent Ions.

The influence of the atmosphere on the mobility is twofold. Firstly, owing to the finite time of relaxation of the atmosphere, a slight *asymmetry* is developed which introduces a retarding *force* on the central ion. Secondly, owing to the *charge* of the atmosphere, an additional (negative) contribution is made to the *velocity* of the central ion. The latter, or " endosmotic " term in the limiting mobility equation increases directly with the valence of the central ion, while the relaxation term increases much less rapidly. This term, which is the smaller even for uniunivalents electrolytes in water, becomes therefore of little importance for high-valent ions. The assumption will be made that it has negligible effect

on the mobility of colloidal ions.  The mobility equation derived by
Onsager [20] is intended only as a limiting law.  Uncorrected application
to reasonable concentrations of very high-valent ions would lead to
absurd negative conductivities : this is mainly because no such term
as the $\dfrac{1}{1 + \kappa a}$ term of the Debye-Hückel formula for log $f$ has been in-
troduced, except in the treatment by Debye and Hückel [21] and Hückel [12]
of the cataphoresis of spherical particles.

The valence of an elementary spherical shell of the atmosphere
of thickness d$r$ and radius $r$ is d$\bar{z}$, given by (7).  If the ordinary hydro-
dynamic laws can be considered applicable, the shell will move according
to Stokes' law with the velocity given by

$$\mathrm{d}V = \frac{x \cdot \epsilon \cdot \mathrm{d}\bar{z}}{6\pi\eta r} \qquad . \qquad . \qquad . \qquad . \quad (26)$$

where $X$ is the field strength and $\eta$ the viscosity, in the absence of any
other source of motion.  Actually all the elementary shells constituting
the atmosphere will move in this way relative to one another and the
central ion itself will move of course in the opposite direction.  The
endosmotic contribution $\Delta V$ of the atmosphere to the velocity of the
central ion will be obtained by integrating (26) from $r = \infty$ to $r = a$,
whence

$$\Delta V = \frac{X\epsilon}{6\pi\eta} \cdot \int_{\infty}^{a} \frac{\mathrm{d}\bar{z}}{r} \qquad . \qquad . \qquad . \qquad (27)$$

It is important to notice that the integral, when multiplied by $\epsilon/D$ gives
the contribution of the atmosphere to the *potential* of the central ion.
The potential and mobility are thus influenced in an exactly parallel
way whatever the distribution of the ions in the atmosphere may be.
This is familiar to all who have used von Smoluchowski's cataphoresis
formula.  Whereas the mobility contribution depends only on the *actual*
state of the ion however, log $f$ is a function of its potential *during a dis-
charging process* as well.  It does not therefore follow that log $f$ and $\Delta V$
will be in all case proportional.

The mobility of the central ion in the absence of the endosmotic
effect would be given by

$$V_0 = \frac{X\epsilon}{6\pi\eta} \cdot \frac{z_k}{a} \qquad . \qquad . \qquad . \qquad (28)$$

The ratio of $V_0$ to the potential of the ion due to its own charge is there-
fore the same as that of $\Delta V$ to the potential due to the atmosphere.
Denoting the former potential by $\psi_{k,a}^0$, we obtain

$$\frac{V_0 - \Delta V}{V_0} = \frac{\psi_{k,a}}{\psi_{k,a}^0} \qquad . \qquad . \qquad . \qquad (29)$$

an equation which enables us to calculate the effect of the atmosphere
on the mobility of the multivalent ion very directly from the graphical
computation of $\psi_{k,a}$.

Combining equations (14) and (29), we obtain

$$\frac{V_0}{V_0 - \Delta V} = \frac{1}{1 + \kappa a}, \quad \text{or} \quad \frac{\Delta V}{V_0} = \frac{\kappa a}{1 + \kappa a} \qquad . \qquad . \quad (30)$$

corresponding to the extended formula of the Debye and Hückel theory
for log $f$, and applicable as long as the ionic strength principle holds.

[20] Onsager, *Physik. Z.*, **27**, 388, 1926 ; **28**, 277, 1927.
[21] Debye and Hückel, *Physik. Z.*, **25**, 49, 1924.

It should be noted that, while the absolute decrease of mobility $\Delta V$ due to the endosmotic effect will be reduced to $\dfrac{1}{1 + \kappa a}$ of its value in Onsager's equation, its value expressed as a fraction of the "infinite dilution mobility" will be increased by increase of $a$. For an electrolyte of given valence type, *the relative decrement of mobility will be increased by increasing the size of the ions, whereas the decrement of the osmotic or activity coefficient will be decreased.*

## The Magnitude of the Atmospheric Effects in Colloidal Electrolytes.

We have seen that it is possible, particularly in unsymmetrical electrolytes, for both greater and smaller effects than those predicted by the Debye-Hückel theory to appear. It was a matter of some importance to decide into which of these two classes, and whether wholly into either, colloidal electrolytes would fall. Accordingly some computations by Müller's method, making the assumptions already stated with regard to the atmosphere effects on the gegenions and assuming spherical ions and spherically symmetrical atmospheres, have been made. It was found that for a uni-10-valent electrolyte of $a$ value 10 Å. and a uni-20-valent electrolyte of a value 20 Å., the effects at $N/100$ and below are all *less than would be predicted from the Debye-Hückel theory.* The activity coefficient, osmotic coefficient and multivalent ion mobility
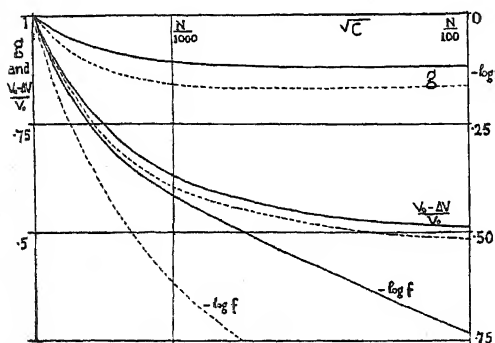


FIG. 5.

for the 1-20 case are shown in Fig. 5. The values obtained from the Debye-Hückel equations are shown by dotted lines. At higher concentrations the deviation from the theory cannot be reversed, and if the values of $a$ are increased, the deviations might at first become greater and later diminish but certainly could not be reversed. The effect of decreasing the valence while keeping $a$ constant will be similar. It was found that the $a$ value for the 20-valent micelle had to be reduced to about 15 Å. before the mobility in $N/1000$ solution became greater than the value obtained from (30), and to about 13 Å. before $-\log f$ became greater than the value obtained from (21). I think it will be agreed that micelles having a more concentrated charge than these are highly improbable, and we may therefore generally conclude that *the atmosphere effects in pure solutions will all be less than would be predicted by the Debye-Hückel theory or equation* (30), taking as $a$ values in these equations the distance of closest approach of the *centres of a micelle and simple ion of opposite charge.* Reference to the $\dfrac{d\bar{z}}{dr}$ curve in Fig. 4 (for the 1-20 electrolyte at $N/1000$) will show that here we have the large increase of this quantity near to the central ion characteristic of

the type of deviation found with very small ions. This is balanced however by the extensive region in which the concentration of micelles has fallen so low that its further decrease cannot appreciably increase its contribution to the charge of the atmosphere. The calculation shows that for the radius taken the latter effect predominates. The effects in excess of univalent electrolytes will probably always be greater than those predicted by the Debye-Hückel theory or equation (30); thus the activity coefficient of an electrolyte, one of whose ions has a radius of 20 Å. present in a small quantity in a uniunivalent electrolyte solution of concentration $N/1000$, was found to be smaller than the Debye-Hückel value for all valences, the values for $- \log f$ for the valence of 20 being 0·335 by the graphical method and 0·265 according to (21). The former value when compared with the value 0·421 for the $N/1000$ solution of the pure 1-20-valent electrolyte (having an ionic strength 10·5 times as great) shows how completely the ionic strength principle fails here.

The conclusion that the effects in pure collodial electrolytes are probably always less than those predicted by the Debye–Hückel equations is of some importance. Until it had been reached several possibilities lay open which must now I think be considered closed. For example, Rysselberghe [4] in the calculations previously mentioned had to assume, in order to account by the Debye-Hückel theory for the observed osmotic pressure, $a$ values for Congo Red and sodium thymonucleate which were already somewhat improbably small. More probable values would have given too high osmotic coefficients even on the simple theory, and his conclusion that what I have called " atmospheric " effects might be a sufficient explanation must therefore be considered unproved. Some form of incomplete dissociation, probably adherence of the gegenions to the micelle by virtue of electrostatic attraction, must be assumed. Again Robinson, in a paper communicated to this meeting (page 245) finds a disagreement between the micellar size for dyes calculated from mobility determinations in the pure solution on the one hand and osmotic pressure and diffusion measurements in the presence of salts on the other, which might, as he points out, have been reconciled if the atmosphere effect on the mobility of the micelle had been very great, and that on the osmotic pressure small. Calculations with the above principle in mind show that, although the mobility of the micelle is the more strongly affected property, the difference cannot be sufficiently great. Attention must therefore be concentrated on the other possible explanations. Finally, the conductivity of long-chain salts may be mentioned : this property shows a very sudden fall on proceeding up the concentration scale at about $N/1000$ in the case of the salts with sixteen carbon atoms in the chain. The evidence discussed in the papers of Murray and Hartley (page 183) and Moilliet, Collie, Robinson and Hartley (page 120) leaves no doubt that this is due to micelle formation and that the micelle is of a predominantly ionic type. Would it be possible for the atmosphere effects alone to produce the fall? The negative answer which the transport number measurements give from the experimental side, can be made even more emphatically now as a result of these calculations,[22]

[22] If the micelle is formed say of twenty long-chain ions with a radius of say 15 Å., it would have a conductivity of 130. This would be reduced by the atmospheric effect to perhaps 70. The equivalent conductivity would therefore still be very much higher than for the unaggregated salt. Thus although the mobility will be reduced much more than the osmotic pressure by atmospheirc effects, the not very great conductivity of these aggregated salts is more difficult to explain than their low osmotic pressure on a purely " atmospheric " theory, because it is raised and not lowered by the aggregation itself.

and again association of the Bjerrum type between micelles and ions must be assumed. The atmosphere effect would, however, provide a satisfactory explanation of the fall in the transport number of the long-chain radical with increasing concentration in the higher concentrations, without necessitating any recourse to the hypothesis of neutral colloid leading an existence independent of the ionic micelle, if the association has reached, in these cases, a limiting value.

## The Association of Gegenions and Micelles.

Bjerrum [13] was able to give his assumption that ions found within the radius where the minimum of the $d\bar{z}/dr$ curve occurs (Fig. 1) should be separately treated as forming an associated pair with the central ion some reasonable physical basis, when he pointed out that the energy necessary to separate ions so close together is more than four times the mean kinetic energy per degree of freedom. If we try to apply some similar consideration to the ionic micelle case, we are met at once with a difficulty that does not appear in the case of the uniunivalent electrolyte. If we are to regard as having a certain probability of associating, any ion which is found so near to another that the work necessary to separate them is a certain multiple of $1/2kT$, it does not very seriously matter whether by " separate " them we mean to some small distance, say 5 Å. apart, where there is a greatly increased probability of their receiving further impulses from the solvent molecules, or whether we mean to separate them to infinity. For example, to separate two univalent ions from, say 1 Å. to 6 Å. requires work equal to $\frac{\epsilon^2}{D}\left(\frac{1}{1} - \frac{1}{6}\right)$, which is not greatly different from that, $\frac{\epsilon^2}{D}\left(\frac{1}{1} - \frac{1}{\infty}\right)$, required to separate them from 1 Å. to infinity. The work required to separate a uni- and a 20-valent ion from 20 Å. to infinity $\left(\frac{20\epsilon^2}{D}\left(\frac{1}{20} - \frac{1}{\infty}\right)\right)$ is about the same as that for the uni-univalent combination separated initially by 1 Å. ; but the work required to separate them by 5 Å. only, is $\frac{20\epsilon^2}{D}\left(\frac{1}{20} - \frac{1}{25}\right)$, only one-fifth as great. In this case therefore what we mean by " separating " the ions matters very greatly. What is significant in connection with the probability of an ion adhering to the micelle is clearly the work required to separate it to such a distance that it is certain to receive further impulses from molecules and be thereby enabled at least temporarily to take its place in the free atmosphere. Whether it receives, when resting on the micelle, the high energy necessary to send it, in the absence of further collisions, to infinity, is of no consequence, because numerous such collisions are bound to occur. An example from an entirely different field may usefully illustrate this point. The energy necessary to take an oxygen molecule from the surface of the earth up into the stratosphere against the force of gravity, is some million times its kinetic energy, but this clearly does not invalidate the ordinary hypsometric law nor cause all the oxygen to be condensed as an adsorbed layer on the ground ; if on the other hand the force of gravity were so great as to cause the molecule to require energy greater than it is likely to receive (instead of a very minute fraction of it) in order to rise from the surface by an amount equal to the mean free path in the air, the situation would be entirely different.

If the energy which has to be supplied to an adherent ion in order to enable it to take part in the external distribution is arbitrarily taken as that necessary to overcome the electrostatic attraction over a distance of 5 Å., this would be about the same as for a uniunivalent combination for which $a$ is about 3 Å., as for a 1-20 combination for which $a$ is 20 Å., but it does not follow that the degree of association in equinormal solutions of such electrolytes would be even of the same order. The volume around the univalent ion in which no point is more than 5 Å from the surface is far smaller than the corresponding volume for the 20-valent micelle, and the *concentration* of oppositely charged ions in this volume will be far greater in the latter case. Thus in $N/1000$ solution the average content of this volume for the univalent case is about 0·003 ions while for the micelle it is about 1·6 ions, *i.e.* there would be about 500 times as many ions available for association with each constituent ion of the micelle as for each ion in the uniunivalent solution. The form of the probability function governing the number of ions which must be adherent to the micelle to maintain equilibrium with the 1·6 ions outside will be moreover highly complicated by factors which could not be taken into consideration by any method which regarded the solvent and micelle as continua—polarisation effects due to the temporary asymmetry of the micelle when an ion approaches very close to it being only one of them. It need not surprise us therefore to find a considerably higher degree of association than would be expected even when the correction due to the increased concentration of ions has been made. It must, however, be realised that this increased concentration in the atmosphere will be a very important factor. Interesting experimental evidence of this is found in the conductivity of long-chain salts in very high fields. A much higher increase of conductivity is obtained than would be expected if the direct atmosphere effect alone were removed : the association is obviously reduced by the removal of the atmosphere. The association of gegenions with the micelle is probably best represented as a combination of an adsorption process with the atmosphere distribution. The concentration at the surface of the micelle relative to the bulk concentration falls with increase of the latter as the atmosphere has more influence on its own distribution (the relative concentrations for $N/100$ and $N/1000$ solutions of the 1-20 electrolytes for which computations were made are 36 and 158), and it would not be surprising to find that the association process showed a saturation effect in solutions sufficiently concentrated.

(*Added in discussion.*) Throughout this paper the simplest possible picture of the micelle and its atmosphere has been assumed—that of perfect spherical symmetry. This picture is taken not on account of its physically plausibility (it is certainly only partly true) but of its mathematical simplicity : if this case can once be worked out it may be possible to adapt it to real cases by subsequent modification. It would be well to indicate what the nature of the modifications necessary on account of temporary asymmetry of the atmosphere might be : as soon as we admit the possibility of this asymmetry, the dielectric properties of the interior of the micelle, which could previously be ignored, must be taken into account, because (fluctuating) fields of force must exist within the micelle. Since this interior will in general have a lower dielectric constant than the solvent (in the case of aqueous solutions of long-chain salts, for example, aggregation only occurs because the long paraffin chains, which constitute the interior of the micelle, are very non-polar

and consequently very insoluble in water) the effect of the asymmetry will certainly be to make the attractive forces for a given configuration of charges greater than they would be if calculated without reference to the dielectric properties of the micelle, and it is to be expected that the difference will be greater for the attraction to the micelle of nearer than of remoter ions. We should therefore expect both " atmosphere " and " association " effects to be increased and the latter more than the former.

## Summary.

The theoretical difficulties in the way of extending the theory of Debye and Hückel to the case of colloidal electrolytes have been discussed.

Calculations have been made by the method of Müller of the magnitudes of the atmospheric effects in solutions of some typical electrolytes. As a result of these it is considered unlikely that, in pure solutions of colloidal electrolytes, activity coefficients smaller than those predicted by the extended equation of Debye and Hückel, or micellar mobilities lower than those predicted by a corresponding equation derived in the paper, will be found.

It is concluded from this that, in order to account for experimental results, some kind of association between micelles and ions of opposite charge must occur. The effect of this on the properties of the solution may be numerically greater than the direct " atmosphere " effects, but it will be considerably modified by them.

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# ARE LYOPHOBIC COLLOIDS COLLOIDAL ELECTROLYTES ?

By Adolph J. Rabinovitch and V. A. Kargin.

## I. THEORY OF COLLOIDAL ELECTROLYTES.

### 1. Historical.

In the historical development of colloidal science two main tendencies characterised the views of investigators who tried to understand the numerous and complicated colloidal phenomena from a broader standpoint.

These tendencies express the physical and chemical aspects of colloidal processes, which in more specialised form may be reduced to the theories of *adsorption* and *dissociation*.

The development of the latter viewpoint led Malfitano [1] and Duclaux [2] to consider colloidal systems as solution of *colloidal electrolytes*, partly dissociated into ions, one being normal, the other, or *colloidal* ion, being abnormally large and having an unusually high number of electrical charges. In recent years, in consequence of the great success of the

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[1] G. Malfitano, *C.R.*, **140**, 1245, 1905.
[2] J. Duclaux, *J, Chim. physique*, **5**, 29, 1907 ; 405, 1909.

adsorptional theories, this point of view seemed to be half forgotten. It was revived by Pauli, who tried in a series of papers and in his well-known book [3] to extend it over the whole domain of colloidal solutions both of lyophilic and of lyophobic character.

Moreover this chemical point of view made great progress especially in the field of typical lyophilic colloids of high molecular weight, such as proteins, dyestuffs, soaps, etc. This was attained mainly by the work of Loeb,[4] who overestimated, however, the bearing of chemical laws on colloidal phenomena, and especially of McBain [5] who showed the applicability of this theory for such typical lyophilic colloids as soap solutions in water.

Serious attempts to construct a full mathematical theory of the dissociation of colloidal electrolytes have been made by Michaelis [6] and Gyemant,[7] these were however based on assumptions of the old theory of dissociation and therefore " must to-day be considered to have failed " as recognised by Michaelis [8] himself. This attempt has been recently reassumed by Linderstrøm-Lang [9] from the standpoint of the new theory of strong electrolytes, but even such typical " colloid electrolytes " as proteins differ in some peculiar respects from ordinary electrolytes.

For lyophobic colloids the views of Michaelis, Gyemant and Pauli and Valkó have mainly to be considered. As said above the two former theories are based upon the old dissociation theory, still valid for weak electrolytes, Pauli and Valkó in their book [3] regard the colloids as being strong electrolytes and accordingly use the conceptions of the new theory of electrolytic solutions. The authors do not attempt, however, to give a strict mathematical theory of colloidal electrolytes and apply the theory of Debye and Bjerrum rather for qualitative considerations.

The part played by Donnan's [10] discovery of the membrane equilibrium in the development of the theory of colloidal electrolytes must not be overlooked. The laws of electrochemistry based on thermodynamics have been shown to hold for colloidal systems with those necessary additions which are connected with the specific properties of these systems.

## 2. Principal Assumptions.

Various assumptions have been made by authors who seek to build up a theory of colloidal electrolytes. Probably not all of these assumptions are necessary, and the theory of the future has to be based on a minimum of assumption.

We shall briefly review the questions which arise when one tries to see whether a given colloidal system or a large group of such systems may be regarded as colloidal electrolytes.

1. **Origin of Electric Charge.**—The theory of colloidal electrolytes arose historically, when the chemical point of view on colloid systems sought to explain the origin of electric charges on a colloidal particle as the result of electrolytic dissociation of molecules or complexes which enter the surface of the particle. Various assumptions have been made

[3] Wo. Pauli and E. Valkó, *Elektrochemie der Kolloide*, 1929.
[4] J. Loeb, " Proteins and the Theory of Colloidal Behaviour."
[5] J. McBain, see *e.g.* in Jerome Alexander, *Colloid Chemistry*, **1**, 137, 1926.
[6] L. Michaelis, *Biochem. Z.*, **196**, 83, 1920.
[7] A. Gyemant, *Kolloid Z.*, **33**, 9, 1933.
[8] L. Michaelis in Jerome Alexander, *Colloid Chemistry*, **1**, 493, 1926.
[9] K. Linderstrøm-Lang, *C. R. Lab. Carlsberg*, **15**, No. 7, 1924; **16**, No. 6, 1926.
[10] F. G. Donnan, *Z. Elektrochem.*, **17**, 72, 1911.

as to the nature of the forces connecting these ion-originating ("ionogenic") molecules or groups with the residue of the particle which need not to be analysed in the present paper.

However, at the time when the physical point of view based on adsorption was prevalent it was understood that the charges on the particles of colloids may have another origin than stated above, without excluding the possibility of their being treated as colloidal electrolytes. The new conception of the origin of the charge was that it is due to the unequal adsorption of the ions of electrolytes by colloidal particles. Those ions which are adsorbed in larger quantity owing to their higher adsorption potential, form the *charging ions* (*aufladende Ionen* according to Pauli), their partners remaining in larger amount in the intermicellar liquid as compensating ions (*Gegenionen* of Pauli). The excess of one kind of the ions on the surface determines the sign of the charge and its density.

In the further development of the theory this clear and simple picture has been altered by an additional assumption (which seems to be unnecessary for the maintenance of the theory of colloid electrolytes) that of the two kinds of ions of the electrolyte present, one kind is totally adsorbed, the other remaining in the intermicellar liquid. To this end we have to assume an infinitely high value of the adsorption potential of the surface towards one kind of ions of the electrolyte. This hypothesis seems to be not only unnecessary but also incorrect, as experimental investigations (see below) frequently show a certain concentration of charging ions in the intermicellar liquid.

In an important paper [11] Linderstrøm-Lang showed that the same result ought to be reached whether we start from the laws which determine the state of the molecules and follow the effect of increasing the size of the molecules up to the magnitude of protein complexes, or whether we start from the laws prevailing at interfaces and gradually decrease the size of the interface.

This once more showed that no profound discrimination can be traced between the physical and chemical views, between the theory of adsorption and that of dissociation.

**2. Applicability of Mass Action Law.**—Some form of the mass action law has been supposed to hold for colloidal electrolytes, so far as they have been treated from the standpoint of the classical dissociation theory. This is still required so long we regard them as weak electrolytes. There are, however, theoretical objections ; the whole mass of the particle does not take part in determining the equilibrium which is reached at the surface of the particle. Account must be taken of the fact that we are dealing with a multi-phase system, and corresponding corrections have to be introduced. This has been emphasised in many papers and especially in a recent paper [12] by Mukherjee.

**3. Osmotic Pressure.**—Peculiar corrections must also be introduced when calculating the osmotic pressure of colloidal electrolytes, whose single ion is a gigantic micellar ion. Not all the observed phenomena, *viz.* Hammarsten effect, could be explained without introducing special assumptions.[13]

**4. Ionic Activity and Conductivity.**—Many attempts have been made to show that the same relations exist between these two characteristic magnitudes in colloidal electrolytes as those which exist for ordinary electrolytic solutions. In some cases this had been proved, but the number of discrepancies (especially for lyophobic colloids) is so large that it induced Mukherjee [12] to speak of a quite different (*eigengesetzlich*) behaviour of colloids in comparison with the ordinary electrolytes. Pauli and Valkó [14] answered this paper by Mukherjee but they could not adduce any stronger

[11] K. Linderstrøm-Lang, *C. R. Lab. Carlsberg*, **15**, No. 7, 1924.
[12] J. Mukherjee, *Kolloid Z.*, **62**, 257, 1933.
[13] K. Linderstrøm-Lang, *C. R. Lab. Carlsberg*, **16**, No. 6, 1926.
[14] Wo. Pauli and E. Valkó, *Kolloid Z.*, **66**, 312, 1934.

argument in favour of the theory than to express the hope that the dis-crepancies existing to-day will vanish some time, just as some difficulties connected with the osmotic pressure of lyophilic colloids vanished when the Donnan membrane-equilibrium was applied for the treatment of these cases.*

**5. Solubility Product and Theory of Coagulation.**—There have been some attempts to regard the process of coagulation as the result of attaining the solubility product of the ions of the stabilising electrolyte and of that producing coagulation. However, this hypothesis in its simplest form was not experimentally verified, at any rate for lyophobic colloids.[15]

**6. Colloidal Electrolytes and Double-Layer Theory.**—Whilst formerly the Helmholz-Smoluchowski double-layer theory developed by Gouy, Chapman, Stern, Müller and others, seemed to be contradictory to the theory of colloidal electrolytes founded on the classical theory of the dissociation of weak electrolytes, the new development of the theory of electrolytes (which takes into account the interionic forces) gave, in prin-ciple, the same picture of the distribution of ions of one sign around an ion of the opposite sign as is accepted in the classical theory of the diffuse double layer. This development had the effect of drawing the theory of colloids and that of electrolytes nearer to each other than they ever have been.

### 3. Present State of Theory.

We have just seen that all the assumptions of the theory of colloidal electrolytes do not hold, especially for lyophobic colloids, and, moreover that there does not exist to-day a real theory of colloidal electrolytes presenting a chain of logical statements formulated in strict mathema-tical form, permitting of quantitative prediction of colloidal phenomena. Such a theory has yet to be constructed and many authors who regard colloids as electrolytes seem themselves somewhat sceptical when esti-mating the present day achievements of the theory, especially in its application to lyophobic colloids.

Let us quote only a few opinions :—

Kruyt says [16] : "It is obvious that there is an enormous difference between the electrical behaviour of a suspensoid particle and an ion of an electrolyte in a true solution. When dealing with true solutions of electro-lytes we never find that an aluminium ion has 500 times the influence of a sodium ion nor has fuchsine ion ever 10,000 times the effect of a potassium ion ; with these characteristic disproportionalities we deal only in the cases of colloidal stability and of capillary electric phenomena."

We cited on page 51 the opinion of Michaelis [6] according to which his own theory of colloidal electrolytes and that of Gyemant [7] must to-day be considered to have failed.

And even Pauli and Valkó [14] write in their reply to the paper of Mukherjee [12] : "We agree with Mukherjee that the conception of dissocia-tion constants, of activity or of solubility product of a colloidal electrolyte meet difficulties in the sense of thermodynamics. It is remarkable that Mukherjee himself confines these difficulties partly to anorganic colloids. As a matter of fact, it has been possible to apply these conceptions in strict

* It is to be observed that some considerations of Mukherjee [21] regarding the properties of colloidal acids are incorrect, being based upon an interpretation of experimental data obtained previously in our laboratory ; an interpretation which we do not believe to-day as correct, although the data themselves are ab-solutely reliable. Our new interpretation of these data is given in our second paper.

[15] See *e.g.* F. Usher, *Trans. Faraday Soc.*, **21**, 406, 1925 ; A. J. Rabinowitsch und Dorfmann, *Z. physik. Chem.*, **131**, 313, 1928.

[16] H. R. Kruyt, *Colloid Symp. Monogr.*, **5**, 7, 1928.

thermodynamical meaning to soaps [5], [13] and up to a certain extent also to proteins.[17] They become however unwieldy in respect to the majority of anorganic colloids in consequence of the plurality of chemical individuals which are in equilibrium with each other. Therefore, preference must be given for the treatment of these systems to molecular-kinetic considerations rather than to thermodynamical ones."

## II. SOME FACTORS BEARING UPON THE THEORY OF COL-LOIDAL ELECTROLYTES AS APPLIED TO LYOPHOBIC COLLOIDS.

If a complete theory of colloidal electrolytes applied to lyophobic systems is to be constructed it will have to take in account some factors we do not meet in solutions of ordinary electrolytes : the di- or polyphasic character of colloid systems, the presence of interfaces, the polyvalence of colloid ions, the complete asymmetry of the colloidal electrolyte, the fact that not all the mass of the colloidal substance contributes towards defining the equilibrium as the latter is attained on the surface of the particles.

To these and other factors already stated by previous authors we should like to add a few others which ensue from investigations on lyophobic colloids carried out in our laboratory.

### 4. Dilution of Colloidal Acids.

The discordance existing between electrolytes in true solution and colloidal electrolytes may be well illustrated by the peculiar behaviour of the latter when colloidal solutions of acid character are considerably diluted by water. Our attention was called to this subject when investigating the electro-chemical properties of colloidal silica.[18] These sols prepared by Graham's method and electrodialysed showed high acidity. The amount of free hydrogen ions (determined by conductometric and potentiometric methods which gave consistent results) proved to be 80 per cent. or more of the total H-ion content of the sol, as found by conductometric titration with caustic soda. On dilution a remarkable increase in the acidity was found : the apparent " degree of dissociation " increased rapidly to 100 per cent. and starting from a dilution of sixteen times grew larger than unity, attaining 330 per cent. at a dilution of 128 times. Later experiments quoted more in detail in our second paper [19] proved that practically the whole acidity of silica sols is due to hydrochloric acid intimately connected with the $SiO_2$-particles and that therefore silica sols are not suitable for the investigation of colloidal acids.

Another series of experiments has been made by the present authors [20] on the dilution of $WO_3$ and $V_2O_5$ sols.

Characteristic curves have been obtained when plotting the $p_H$-values of the diluted sols against the dilutions or, better, the $\log_2$ of dilution (see Fig. 1).

The $p_H$ rose with increasing dilution more slowly than would be expected for an acid in true solution. Beginning with dilution 64 the $p_H$-value remains practically constant, i.e., the colloid behaves

[17] Wo. Pauli and E. Valkó, *Kolloidchemie der Eiweisskörper*, 1933.
[18] A. J. Rabinowitsch and E. Laskin, *Z. physikal. Chem.*, **134**, 387, 1928.
[19] V. A. Kargin and A. J. Rabinovitch, see this Discussion, page 284.
[20] A. J. Rabinowitsch and V. Kargin, *Z. physikal. Chem.*, A **152**, 24, 1931.

like a buffer solution. A rapid growth of $p_H$ begins again after dilution 4000 is reached. This peculiar form of the dilution curve has been explained in the following way. With progressive dilution colloidal particles are dissolved, *i.e.* pass into true solution. The dissolution proceeds from the surface of the particles, and the particles gradually diminish in size with increasing dilution. This increase in dispersion is followed by the increase of solubility. When practically all the particles are in true solution (after 4000-fold dilution), the concentration of H-ions decreases on further dilution, and the $p_H$ rises again. The dissolution of the particles is a time process. Immediately after dilution the sols give a marked Tyndall effect, which gradually diminishes but does not vanish; 10,000-fold dilution gave also a weak Tyndall effect, which disappeared after twenty-four hours, showing that all the particles were now in true solution.

Colloidal vanadic oxide was investigated by the same authors (with glass electrodes for $p_H$ determinations), and absorption spectra were used to follow the gradual hydration of red $V_2O_5$ into colourless vanadium compounds. The results are here much more complicated than in the case of $WO_3$ sols, as $V_2O_5$ passes into true solution through a long series of polyvanadic acids of various degrees of hydration. In this case also gradual dissolution of colloidal particles has been proved.



FIG. 1.

The behaviour of those acid sols where the acidity is not inherent to the colloidal particles but is caused by the presence of strange electrolytes, partly adsorbed on these particles is quite different. As examples of such sols arsenic trisulphide and ferric oxide may be cited. (In the case of $Fe_2O_3$ sols $p_{Cl}$ was measured instead of $p_H$.) Here the dilution curve is nearly rectilinear, slight deflections from the straight line being readily explained by hydrolysis.

In a recent paper Mukerjee[21] analysed the relations existing in diluting colloidal acids and found the mass action law to be inapplicable in these cases, since the mass of the acids in the interior of the colloidal particles is unavailable for equilibrium: only surface molecules of the particles are in equilibrium with the dissolved acid in the intermicellar liquid. Therefore the degree of dissociation, the dissociation constant, solubility and similar magnitudes have another sense than in true electrolytic solutions.

## 5. Significance of Potentiometric Measurements in Colloidal Systems.

Potentiometric measurements of ionic concentration using reversible electrodes of the first and second kinds and, especially, potentiometric
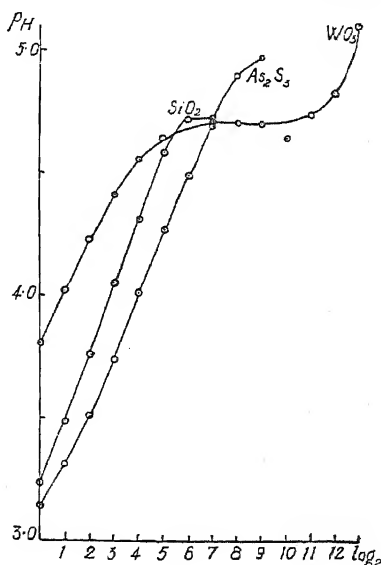
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[21] J. Mukherjee, *Kolloid Z.,* **67,** 178, 1934.

titration curves which permit us to follow ionic concentration changes in various colloidal processes (*e.g.* coagulation, peptisation, etc.) are valuable methods introduced and extensively used in the field of colloid chemistry by Pauli and co-workers [22] and, independently, by the present authors.[23] In later years these methods have been developed and applied by many other authors.[24] So many have been the applications of this measuring technique, and so important the conclusions drawn from it as to the mechanism of various colloidal processes, that a brief theoretical discussion of the principles underlying this method and of the strict sense of the obtained numerical values seems desirable, especially as a certain vagueness seems to exist on this point in many papers.

The main assumption underlying most potentiometric investigations is that the potentiometrically measured ionic concentration represents the mean concentration of compensating ions, *i.e.* of ions of sign opposite to that of the particle surrounding the latter in the double layer. We intend by the term " *mean* " a certain mean value of concentration obtained from the concentration of these ions in the intermicellar liquid and in the double layers.

We can trace this conception as far back as to the early paper by Pauli and Matula [25] on ferric oxide sols, where concentration of Cl- and H-ions were measured by means of calomel and hydrogen electrodes. Unfortunately, as a result of an error of method no particular concentration of H-ions could be stated : the sols appeared nearly neutral, owing to the poisoning of the Pt electrode in colloidal ferrioxide as shown later in our laboratory.[26] From the absence of free hydrogen-ions it was concluded that the whole amount of the determined Cl-ions belonged as partners to the colloidal particles of $Fe_2O_3$, acting as though they were compensating ions (*Gegenionen* according to Pauli). The number of these ions gave consequently the sum of the electric charges on the particles and allowed Pauli to find the values of the so-called *colloidal equivalent, i.e.* the ratio of the number of molecules entering a colloidal particle to the number of electrical charges on its surface.

These values varied to a large extent for various sols of the same substance, which seems rather strange (especially for colloidal silica if we accept the scheme of its structure advanced by Pauli).[27] Moreover, the values of colloidal equivalents gave in most cases very high densities of the charge on colloidal particles, not readily compatible with measurements of double layer capacity.

Usher [15] found for gamboge sols a large discrepancy between the density of the charge determined by the cataphoretic method ($10^{-8}$ e.s.u. per particle) and that obtained by other methods ($1·5 . 10^{-3}$). This discrepancy is characteristic, also, of the potentiometric method, which

[22] Wo. Pauli and E. Valkó, *Elektrochemie der Kolloide*, p. 294.

[23] (*a*) A. J. Rabinowitsch and R. Burstein, *Biochem. Z.*, **182**, 110, 1927; (*b*) A. J. Rabinowitsch and V. Kargin, *Z. physik. Chem.*, **133**, 203, 1928 ; (*c*) E. Laskin, *Kolloid Z.*, **45**, 130, 1928 ; (*d*) A. J. Rabinowitsch and V. Kargin, *Z. physikal. Chem.*, A **143**, 21, 1929 ; (*e*) V. Kargin, *Kolloid Z.*, **49**, 281, 1929. (*f*) A. J. Rabinowitsch and E. S. Awtonomowa, *Kolloid Z.*, **55**, 207, 1931 ; (*g*) P. S. Wassiliev and A. J. Rabinowitsch, *Kolloid Z.*, **56**, 305, 1931 ; (*h*) A. J. Rabinowitsch and E. Fodiman, *Z. physik. Chem.*, A **159**, 403, 1932 ; (*i*) A. J. Rabinowitsch and V. Kargin, *Z. physik. Chem.*, A **152**, 24, 1931.

[24] H. Freundlich, K. Joachimsohn and G. Ettisch, *Z. physik. Chem.*, A **141**, 249, 1929 ; H. B. Weiser, *J. Physic. Chem.*, **36**, 2796, 1932.

[25] Wo. Pauli and J. Matula, *Kolloid Z.*, **21**, 49, 1917.

[26] A. J. Rabinowitsch and V. Kargin, *Z. physik. Chem.*, **133**, 203, 1928.

[27] Wo. Pauli and Valkó, *Kolloid Z.*, **36**, *Erg. Bd.*, 352, 1925.

usually gives very high values of ionic concentrations incompatible with the low charge density on the particle.

A still more radical view on the significance of values obtained by potentiometric methods was put forward by Wiegner [28] who supposed that not only may the ions entering the outer part of the double layer act upon an electrode but also those which are attached to the particle itself being adsorbed in the inner part of the ionic double layer.

A short theoretical discussion shows that the points of view of both Pauli and Wiegner are erroneous: the concentrations of the ions entering both the outer and the inner component of the double layer does not in the slightest degree affect the reversible electrodes dipped into a colloidal solution; these electrodes respond only to the equilibrium concentration in the intermicellar liquid. All the potentiometric measurements have a definite physical meaning only if the determined values correspond to the system in equilibrium. On the other hand, potentiometric determination yield values of *activities*, not of concentrations. For a system in equilibrium the activity of all its parts must be equal. Therefore, if we imagine two " microelectrodes " responding to the compensating ions (one of the electrodes being immersed in the intermicellar liquid, the other being situated in the double layer of some particle), both electrodes must give strictly equal values, although the concentration of the compensating ions is much higher in the double layer. In fact, notwithstanding the great difference in concentration, the *activity* must be equal at every point of the system, the differences in concentration being compensated by corresponding differences in activity factors :

$$c_1 f_a = c_2 f_a{}' = c_3 f_a{}'' = \ . \ . \ . \ Constant \ (1).$$

Assuming that within the intermicellar liquid where no further traces of double layers can be found (let us denote this point as " zero point ") the activity factor attains the value of $f_{a_0} = 1$, the first micro-electrode would measure the ionic *concentration* in the intermicellar liquid, and consequently any other micro-electrode or macro-electrode must yield the same magnitude, *i.e.* the *equilibrium concentration* (with the correction for the activity factor in this concentration) in the intermicellar liquid.

This is a justification of the application of potentiometric measurements for the determination of ionic *adsorption* in colloid systems : only those ions will be measured by the electrodes which, the equilibrium being reached, remain in the intermicellar liquid.

For a schematic " ideal colloidal electrolyte " with motionless particles, whose compensating ions are situated only in the double layer, not entering into the intermicellar liquid, we should receive the above-mentioned activity value equal to zero, as the concentration of these ions in the " zero point " of the solution is zero. From this we come to the somewhat paradoxical conclusion that the activity of the compensating ions in the double layer of such a system would also be equal to zero.

The system pictured above is, however, quite unnatural in the sense that the complete immobility of colloidal particles could only be realised by applying forces directed against the kinetic energy of the thermal agitation of the particles. In such a system the osmotic pressure is zero, which explains the zero value of activity.

[28] G. Wiegner, *Kolloid Z.*, **51**, 49, 1930 ; Pallmann, *Kolloidchem. Beihefte*, **30**, 334, 1930.

In the absence of such imaginary forces, compelling the particles to remain stationary, the system possesses a certain osmotic pressure, determined by the kinetic energy of the thermal agitation. In such a *natural* system the activity connected with the osmotic pressure is no longer equal to zero and the same holds for the activity of the compensating ions.

Thus, in every micro-heterogenous system the activity of the compensating ions is inseparably connected with the activity (*viz.* osmotic pressure) of the particles, depending on their movements and their number, and not merely on their electrical charges.

The activities of compensating ions obtained from potentiometric measurements usually give figures many hundred times exceeding those which can be calculated from the purely osmotic properties (number and size) of the colloidal particles.

### 6. High Equilibrium Concentration of both Ions of Peptising Electrolyte.

It has been shown in the last paragraph that a large discrepancy exists between the number of compensating ions as found from osmotic calculations and the number as determined from potentiometric measurements.

The simplest explanation of this discrepancy is given by the assumption that potentiometric determinations yield too high figures, since they take into account not only the true compensating ions but all the ions of the same kind present in the intermicellar liquid. The number of the latter may be large, owing to the presence of foreign electrolytes. Such an assumption is of course contradictory to the above traced scheme of an ideal colloidal electrolyte as pictured by Pauli and Valkó. This scheme requires that all the charging ions creating the charge of the colloid particle (inner leaf of double layer) be inseparably connected with the particle, forming a kind of large complex ion. The concentration of these ions in the intermicellar liquid must consequently be equal to zero.

We believe this scheme to be realised in practice only in the case of compounds of high molecular weight (proteins, dyestuffs, soaps, etc.). For the usual lyophobic colloids it can hardly be correct : a definite equilibrium existing between the ions on or around the surface of the particle and the free ions of the electrolyte in the intermicellar liquid.

If the ionic charges on the particles are formed as a result of the adsorption of the peptising electrolyte it is easy to explain this equilibrium as an ordinary adsorption equilibrium ; if the peptising electrolyte forms intermediate chemical compounds with the substance of the colloidal particle, corresponding solution pressures of the components of these compounds must exist in the surrounding liquid. Thus, the presence of *both ions* of the peptising electrolyte in the *intermicellar liquid* is imperative as a principle, independently of the accepted view as to the origin of the charge of colloidal particles.

This point of view cannot have been absent from the mind of Pauli in his first paper [25] on the application of potentiometry. As stated above, an error in method led them to the false conclusion that all the Cl-ions determined are true compensating ions, having charged colloidal particles as partners.

In a series of subsequent papers the same assumption was made by various authors without any attempt to verify it by experiment. Such

are the papers on colloidal silica,[27] arsenic trisulphide, [29, 30] gold [30] and many others.

On the other hand it is well known that most of the colloidal solutions studied contain noticeable quantities of electrolytes in the intermicellar liquid, even if, previously to the measurements, they are submitted to purification by dialysis, electrodialysis, etc.

Thus it was shown by Pennycuick [31] that after removing platinum from a platinum sol by freezing, the filtrate contained a noticeable amount of free acids. Wintgen and Hacker [32] demonstrated that the conductivities of a gold sol, its ultrafiltrate and centrifugate are very near to each other. Pauli and Peters [33] who studied the hydrolysis in a $ThO_2$ sol found it to contain marked quantities of HCl. Considerable amounts of $Ag_2O$ were discovered in silver sols by Einecke [34] and others. Similar observations have been made by Mukherjee [35] on alumina sols, etc.

This question has been experimentally investigated in our laboratory in connection with the problem of equivalency in exchange adsorption. In a previous paper one of the present authors [33] stated that on adding barium chloride to arsenic trisulphide sols, the amount of barium ions adsorbed by the particles is strictly equivalent to the quantity of $H_+$ ions present in the filtrate after coagulation. This was interpreted as regular exchange adsorption, the $Ba^{++}$ ions substituting the $H^+$ ions in the double layers surrounding the particles. In a series of subsequent papers many cases of exchange adsorption of ions in colloids have been investigated in our laboratory. In all the cases where the amount both of adsorbed and of replaced ions could be determined, deviations from equivalence have been found: for lanthanum in mastic sols,[23] (a) for silver ions in tungsten trioxide and titanium dioxide sols,[23] (f) for dyestuffs [18] and barium [37] in silica sols. The same has been stated by Freundlich and co-workers [30] for various cations in arsenic trisulphide and gold sols. In a recent paper Weiser [24] studied again arsenic trisulphide sols and found that metals of alkaline earths replace hydrogen ions in non-equivalent amounts.

Kargin and Klimovitzkaja in our laboratory took up this subject and confirmed the experimental results of Weiser except for barium, where equivalence was found, in agreement with the previous data of Rabinovitch.[36] Some of these data are summarised in Table I. obtained

TABLE I.

| | Cation Adsorbed in gr.-equ./l. | [H$^+$] in Filtrate in gr.-equ./l. |
|---|---|---|
| Ba | $9.4 \times 10^{-4}$ | $10.1 \times 10^{-4}$ |
| Ca | $7.7 \times 10^{-4}$ | $9.8 \times 10^{-4}$ |
| Mg | $6.5 \times 10^{-4}$ | $9.8 \times 10^{-4}$ |

[29] Wo. Pauli und A. Semler, *Kolloid Z.*, **34**, 145, 1924.

[30] H. Freundlich, K. Joachimsohn and G. Ettich, *Z. physik. Chem.*, A 141, 249, 1929.

[31] S. W. Pennycuick, *J. Chem. Soc.*, 2108, 1928.

[32] R. Wintgen and W. Hacker, *Kolloid. Z.*, **61**, 335, 1932.

[33] Wo. Pauli and A. Peters, *Z. physik. Chem.*, **135**, 1, 1928.

[34] E. Einecke, *Z. analyt. Chem.*, **89**, 90, 1932.

[35] J. Mukherjee, *Kolloid Z.*, **63**, 36, 1933.

[36] A. J. Rabinowitsch, *Z. physik. Chem.*, **116**, 97, 1925.

[37] See [23] (a), (f), (c) ; Z. Berestneva and V. Kargin, *in the press*; V. Kargin and H. Klimovizkaja, *in the press*.

on a sol containing $12\cdot5$ gr. $As_2S_3$ per litre.   The initial concentration of the salts was $2\cdot10^{-3}$ gr.-equiv./l.

The $H^+$ ion content in the filtrate after coagulation was in all cases practically equal to the total $H^+$ content of the sol (let us denote it $h_t$) determined by potentiometric titration with alkali ($h_t = 1 \times 10^{-3}$).

The investigation of the ultrafiltrates of $As_2S_3$ showed them to contain considerable amounts of free acids, mainly arsenious acid, whose presence explains the high acidity of arsenic trisulphide sols.   The above-mentioned colloid was $5 \times 10^{-4}$ $N$ relative to H ions.   These acids give with the cations of alkaline earths difficultly soluble salts, which can be easily observed by adding solutions of corresponding salts to the ultrafiltrates : $e.g.$ $BaCl_2$ gives a white precipitate.   It is natural that in all these cases the acidity of the ultrafiltrate is the same, as is always the case in exchange reactions between salts and acids ;   the concentration of $Ba^{++}$ decreases as a part of these ions is removed from the solution in form of an insoluble salt.

The same process takes place when adding electrolytes to $As_2S_3$ sols.   This results in an apparent " adsorption " of the cation ;   the acidity of the filtrates remains equal, the apparent adsorption of the cations varies in dependence on the solubility of the salts which they form with the acids contained in the intermicellar liquid.

TABLE  II.

| | Cation Adsorbed in gr.-equ./l. | [H⁺] in Filtrate in gr.-equ./l. |
|---|---|---|
| Ba | $10\cdot4 \times 10^{-4}$ | $1\cdot29 \times 10^{-3}$ |
| Ca | $6\cdot6 \times 10^{-4}$ | $1\cdot26 \times 10^{-3}$ |
| Mg | $3\cdot7 \times 10^{-4}$ | $1\cdot25 \times 10^{-3}$ |

Analogous facts have been found in the investigation of vanadium pentoxide sols by the same authors.

The sol contained $3\cdot35$ gr./l $V_2O_5$.   Total acidity $h_t = 1\cdot20 \times 10^{-3}$, acidity of ultrafiltrate $-1\cdot91 \times 10^{-3}$.   By adding $BaCl_2$ to the ultrafiltrate, a precipitate is formed, similarly to what has been said on colloidal $As_2S_3$.   Contrary to the latter the acidity of the filtrate exceeds that of the sol.   This may be explained by the relatively high solubility of the $V_2O_5$ particles, which allows additional amounts of vanadic oxide to go into solution when part of dissolved acid is removed as insoluble salt.

As seen from the above data, in addition to the possible adsorption of added cations, a process of salt formation takes place in $As_2S_3$ and $V_2O_5$ sols, which is governed by the composition of the intermicellar liquid.   For sols with relatively soluble particles, $e.g.$ $V_2O_5$, it may be expected that the process of salt formation will considerably prevail over the adsorption, especially in diluted sols (fewer particles, concentration of dissolved acid constant).

## 7. Non-Equivalence of Exchange Adsorption.

A question of great importance for the theory of colloidal electrolytes is concerned with the process of substitution of one electrolyte by another in a colloidal system, which can be observed in connection with coagulation.   It is generally considered as a process of exchange adsorption of the compensating ions in the outer component of the double layer.   The few direct measurements of mutual substitution of ions gave contradictory results.

Cases of non-equivalency have been cited in the foregoing paragraph. More or less strict equivalency has been observed only for arsenic tri-sulphide sols [36, 38] and recently for silver iodide sols by Verwey and Kruyt.[39]   Equivalence of ionic exchange in heterogenous systems has been found by many authors.

Taking into account the process of salt formation which we em-phasised above, these results cannot be used for the formulation of an opinion as to the equivalency or non-equivalency of the ionic interchange in the double layer.   As a matter of fact, upon this process, which in many cases takes place between comparatively limited amounts of ions, another process is superposed—that of formation of salts of various solubility, which proceeds in the intermicellar liquid between large amounts of substance, and in many cases completely obscures the exchange phenomena in the double layer.   From this view-point we may say that up to the present time the available direct ex-perimental data are quite insufficient for the solution of the question of the equivalency or non-equivalency of exchange adsorption of com-pensating ions.   Indeed, of the above-mentioned examples, in the cases of arsenic trisulphide, of gold, of tungsten trioxide, of vanadic oxide and probably also of mastic sols, the process of ionic exchange is com-plicated by the formation of difficultly soluble salts in the intermicellar liquid.   In case of dyestuffs adsorption on colloidal silica we probably have to deal not with ionic but with molecular adsorption.   The increase of $p_H$ (adsorption of H ions) in case of coagulation of positive colloids by electrolytes, observed by many authors, shows that not only the com-pensating ions but also the ions of the same sign as the particles (Pauli's *Gegenionen*) may take part in adsorption processes of coagulation. This may serve as an indirect indication that the process of exchange adsorption is to be accounted for from a more broad point of view, not requiring a strict adherence to the principle of equivalency in the substitution of compensating ions.   Direct indications of the invalidity of this principle were recently obtained in our laboratory, by Z. J. Berestneva, who studied the coagulation of alkaline silica sols by barium salts.   A considerable adsorption of Ba ions ($\sim 10^{-2}$ gr. equiv./l.) is connected with the replacement of very small amounts of H ions ($\sim 10^{-4}$ gr. equiv./l.) the concentration of Na ions remaining practically unchanged.

The scarcity of experimental data makes it impossible to do more than attack the problem of the equivalency of ionic exchange with the aid of theoretical considerations based on definite assumptions on the origin of the charge on colloidal particles.

The equivalency of the exchange adsorption of ions in the double layer may be admitted for typically lyophilic systems which satisfy the definition of colloidal electrolytes.   Their particles form true col-loidal ions with a constant number of charges, and, consequently, a constant number of ions enter the outer component of the double layer.

The requirement of equivalency has to be rejected in the case of typically lyophobic colloids if we take into account that the charge of their particles is originated by an unequal adsorption of different ions of electrolytes present in the intermicellar liquid.

[38] E. S. Linder and H. Picton, *J. Chem. Soc.*, **67**, 63, 1895 ;  W. R. Whitney and J. A. Ober, *Z. physik. Chem.*, **39**, 630, 1902.
[39] E. J. Verwey and H. R. Kruyt, *Z. physik. Chem.*, A **167**, 312, 1934.

Indeed, the constancy of the number of molecules of the substance adsorbed on a given surface forms the main requirement of equivalency in exchange adsorption.

In case of a new substance (an electrolyte) being introduced into the system we have a case of adsorption from a mixture, where, as well known, the number of molecules of the adsorbed substance is not equal to the amount of mols. of each component separately, additivity being, however, not observed.   In other words every introduction of electrolyte shifts the adsorption equilibrium in the system and brings about additional adsorption or desorption of the initial (peptising) electrolyte, together with the adsorption of the newly introduced electrolyte.   In the most general case, the cations, as well as the anions, of both electrolytes (the initial peptising and the added coagulating electrolyte) take part in these processes.

The phenomena described must naturally lead to the non-equivalency of the ionic exchange in coagulation.   These phenomena take place in case of high equilibrium concentrations of adsorbed electrolytes in the intermicellar liquid, the non-equivalency of the exchange being due to the change of the equilibrium concentration of the initially adsorbed substance.

But in cases where the equilibrium concentrations in the intermicellar liquid are practically equal to zero or where the adsorption saturation of the surface by the initial substance is reached an equivalent substitution by another substance may be expected.   Such cases may be realised in macro-heterogeneous systems.   As to the lyophobic colloidal systems, the first case has not been observed among the sols examined, the second is unrealisable on account of the inevitable precipitation of the sol at electrolyte concentrations corresponding to the adsorption saturation.

## 8. Variability of Charge and of $\epsilon$- and $\zeta$-potentials.

The non-equivalent substitution of one adsorbed substance by another must inevitably lead to a change in the number of charges connected with the particle and consequently to a considerable change in the total ($\epsilon$-) potential, due not only to the change in the capacity of the double layer (this is assumed by many authors) but to the change in the number of ions on the surface of the particle as well.

Changes of the total ($\epsilon$-) potential depending on the surrounding electrolyte have been experimentally found by Lengyel [40] on quartz.

The change in the total electric potential difference ($\epsilon$-) between the particle and the intermicellar liquid naturally involves the change of the $\zeta$-potential—the potential difference on the surface (*Abreissfläche*) dividing the liquid moving with the particle from the rest of the liquid of the colloidal system.   Indeed, the $\zeta$-potential is determined not only by the distribution of the charges in the double layer, but in the first place by their absolute number.

The above developed conceptions of the presence of considerable equilibrium concentrations of both ions of the electrolyte in the intermicellar liquid of the majority of lyophobic colloid systems lead to a somewhat altered picture of the structure of the electric double layer and of the origin of the $\zeta$-potential difference.

So far as the two ions of the electrolyte are present in the intermicellar liquid as well as on the surface of the particle, the latter must

[40] Bela Lengyel, *Z. physik. Chem.*, **159**, 145, 1932.

possess a positive adsorption potential in regard to the two ions of the electrolyte, notwithstanding that their signs are different. This leads necessarily to the distribution *of the two* ions in the double layer being determined by the values and spatial distribution of specific and electrostatic potentials for the two ions. Whereas Pauli's theory of colloida electrolytes considered exclusively the spatial distribution of the ions having a sign opposite to that of the colloid particle (*Gegenionen*) and on this ground defined the $\zeta$-potential, our above-mentioned considerations require the distribution of *both* ions to be taken into account, which considerably complicates the definition of the $\zeta$-potential. Thus, the calculations of the $\zeta$-potential made by Müller [41] and others (based upon an idealised scheme of the colloidal electrolyte, assuming constancy of the charge-number on the colloidal particle and absence of charging ions in the intermicellar liquid) do not correspond to the actual conditions in colloidal systems.

## 9. Consequences for the Theory of Coagulation.

A few factors have been mentioned above, deduced partly from new experimental data partly from general considerations, which ought to be taken in account when attempts will be made to build up a complete theory of colloidal electrolytes in its application to lyophobic colloids.

It will shortly be pointed out what bearing these factors may have on the theory of coagulation by electrolytes, this being one of the most important colloidal processes.

As stated in previous papers from our laboratory [42] we believe the adsorption of ions of opposite sign to the particle to be one of the main factors in diminishing the stability of the colloid and causing its coagulation. When ions of higher valency, of larger specific adsorption potential, than the initial compensating ions are adsorbed, they enter the inner part of the outer component of the double-layer. This diminishes the number (density) of electric charges on the boundary between the liquid moving with the particle and the rest of the liquid and consequently the electrokinetic or $\zeta$-potential on this surface. The latter being a more or less accurate quantitative measure of repulsive forces between the particles, these forces decrease too, and the stability of the system breaks down.

Now, owing to the experimental data and considerations advanced in the present paper we must add to this picture some features which render it more complicated, but probably more in accordance with reality.

Attention has been drawn above to the presence of both ions of peptising electrolyte in the intermicellar liquid which leads to the *formation* of difficultly soluble *salts*, with the electrolyte added for coagulation. As a result of this, more or less considerable amounts of peptising electrolyte are removed from the intermicellar liquid. The adsorption equilibrium is shifted, a desorption of peptising electrolyte from the particles takes place, and the stability of the colloidal system is diminished, sometimes leading to coagulation.

These phenomena are probably the cause of the characteristic form exhibited by the curves expressing cataphoretic velocity as a function of the electrolyte concentration. They drop abruptly in the beginning

[41] H. Müller, *Kolloidchem. Beihefte*, **26**, 257, 1928.
[42] A. J. Rabinowitsch, *Sow. Physik. russ.*, **4**, 34, 1933.

and become far less steep for higher electrolyte concentrations. The abrupt decrease of cataphoretic velocity at small concentrations must correspond to the stage of salt-formation : the end of the rapid fall coincides with the total acidity of the sol as shown by Pennycuick [43] for platinum sols and by Rabinovitch and Fodiman [44] for arsenic trisulphide sols. After this point is attained no more materials for salt formation are available.

Another factor of great importance, especially in those cases where no insoluble salts are formed, is the *adsorption* of the electrolyte added for coagulation. It must now be considered from a standpoint differing from the old views on exchange adsorption. *Both ions* of the introduced electrolyte may be adsorbed by the particle, one of them diminishing, the other increasing its charge and stability. At the same time the adsorption of both ions of the initial stabilising electrolyte is influenced by the addition of the new electrolyte. It is a matter of balance between the adsorption potential of the surface towards these four kinds of ions, whether the stability of the colloid will increase or diminish after adding a new electrolyte. Increase of stability and cataphoretic velocity has been found by addition of KCl to arsenic trisulphide [45] and selenium sols,[46] of $Na_2SO_4$ to ferric oxide sols,[26] etc.

This conception of " exchange adsorption " in a broader form leads to the necessity of considering the change not only of repulsive but also of *attractional* forces which the colloidal particles may exert on each other. In fact, we depart from the current conception of a colloidal particle as a multivalent ion with a constant number of charging ions ; all the ions of the electrolytes present may be adsorbed by the surface of the particle, and not merely enter the outer part of the double layer. The surface itself must be variable, and the variability of attractive forces towards other particles must be the result of this.

## III. CONCLUSIONS.

Some experimental observations have been reported and discussed in this paper which show that factors exist for lyophobic colloidal solutions which are not met with in ordinary solutions of electrolytes and which have not previously been mentioned by other authors.

The very peculiar behaviour of colloidal acids on dilution, based upon the colloidal particles acting as a reservoir of acid material gradually emptied as dilution is going on, is a good example of such factors.

Our analysis of the meaning of potentiometric measurements in colloidal solutions leads us to the conclusion that these measurements characterise only the equilibrium-concentration of the respective ion in the intermicellar liquid and do not allow any conclusion as to its concentration in the double layer. This means that all potentiometric determinations of " compensating ions " are concerned not with the compensating ions in the proper sense of the term (*i.e.* ions in the outer component of the double layer), but with free ions of the stabilising or coagulating electrolyte in the intermicellar liquid. Thus the abnormally high values for the concentration of " compensating ions " are explained.

[43] S. W. Pennycuick, *Kolloid Z.*, **54**, 21, 1931.
[44] A. J. Rabinowitsch and E. Fodiman, *Z. physik. Chem.*, A **154**, 255, 1931.
[45] H. R. Kruyt and van d. Willigen, *Z. physik. Chem.*, **130**, 170, 1927.
[46] D. R. Briggs, *J. Physic. Chem.*, **34**, 1326, 1930.

At the same time our potentiometric measurements and direct analytical determinations showed considerable amounts of stabilising electrolyte to be present in the intermicellar liquid of many typical lyophobic colloids. This results in many cases in the formation of difficultly soluble precipitating compounds, shifting the adsorption equilibrium on the particles and leading to coagulation.

Indications from various scientific papers and our own experimental results have been brought forward for the consideration of the pheno-menon of exchange adsorption. It has been shown that equivalency must not be required generally from the standpoint of the exchange of electrolytes, not only of ions of the same sign.

From these considerations conclusions have been drawn to the vari-ability of the number of electric charges on a colloidal particle, leading to the variability of total ($\epsilon$-) and electrokinetic ($\zeta$-) potentials. These considerations present especial interest for the theory of colloidal elec-trolytes.

A picture of the coagulation process has been given in the light of these new facts and considerations. It has been emphasised that a change not only of repulsive but also of attractional forces must be considered in course of the coagulation. This follows from the vari-ability of the surface of the particle itself when adding new electrolytes. Previous theories of coagulation omitted this factor.

If now we put again the question of the title : " Are lyophobic colloids colloidal electrolytes ? " we have to answer that this question cannot be solved to-day on the basis of the available data. We have not found any theoretical presumptions against treating colloids as elec-trolytes. We must state, however, that this theory presents great difficulties when applied especially to lyophobic colloids.

In addition to those factors discriminating between colloids and elec-trolytes which have been pointed out by previous authors some of the data and considerations advanced in this paper have to be taken in account when attempts are made to build up a complete theory of col-loidal electrolytes applicable for lyophobic colloids.

## Summary.

1. A short historical notice and a restatement of the main assumptions of the theory of colloid electrolytes has been given.

2. It has been pointed out that peculiar properties characterise colloidal solutions not met with in ordinary solutions of electrolytes.

3. In addition to the factors of discrimination between the two kinds of solution emphasised by previous authors a few factors have to be con-sidered which have been found in our laboratory.

4. The peculiar behaviour of colloidal acids in the course of dilution giving them the properties of a buffer solution is one of these factors bearing upon the theory of colloidal electrolytes.

5. It has been shown that potentiometric measurements of ionic con-centration in colloid solution give only the equilibrium concentration of the electrolyte present, and are incapable of determining the concentration of compensating ions.

6. Considerable amounts of both ions of stabilising electrolytes have been detected in the intermicellar liquid of most lyophobic colloids.

7. Insoluble salt formation may occur on adding electrolytes which must influence the stability of the colloidal system.

8. Exchange adsorption of ions has been treated as exchange adsorption of electrolytes with different adsorption potentials for each ion. From this standpoint equivalence is not obligatory in exchange adsorption.

3

9. The number of electric charges on the particles and the total ($\epsilon$-) potential may vary in course of coagulation, not only the electrokinetic ($\zeta$-) potential.

10. Attraction forces between the particles may vary with changing electrolyte concentration as well as the repulsive forces.

11. The bearing of these factors has been shown upon the theory of colloidal electrolytes. Such a theory does not exist to-day, but attempts have to be made to build it up, taking into account all the named factors which cause differences between colloids and ordinary electrolytes.

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　*Karpov-Institute of Physical Chemistry,*
　　*Moscow, U.S.S.R.*

## GENERAL DISCUSSION.*

**Professor E. J. Bigwood** (*Brussels*) said : Professor Kruyt said that colloids were always to be considered as polymolecular products of aggregation, and that this was the criterion of the colloidal condition. It seems to me that the only fundamental basis for a general definition of colloidal particles must be confined to a question of size of the particles conferring certain physical properties such as slow diffusion, Tyndall effect, non-dialysability . . . etc. . . ., and this, independently of the nature of the chemical constitution of the particle. It would be dangerous to decide that a particle must be necessarily an aggregate whenever it shows evidence of the fact that the particle is large. In the case of proteins for instance, there are substances for which there is no evidence allowing for the assumption that one is dealing with aggregation.

Professor Kruyt said that the electrolytic theory is less fruitful than the surface adsorption theory for further investigation in the study of colloids. It seems to me that this statement is certainly not justified, so far as many lyophilic colloids are concerned. Particularly in the case of proteins, the electrolytic theory has given us a much better insight into their chemical properties.

At the end of his report, Professor Kruyt says that ". . . there is no doubt that its inner layer " (of the electric double layer at the surface of a micelle) " is often built up of ions of the material of the particle itself, or at least by ions which belong homogeneously to the particle. However, another architecture is not only possible, but even always present." I believe there is in my own report, experimental evidence of the fact that. in at least a certain range of $p_H$ values, proteins behave exclusively as electrolytes, even when the protein is in the gel state.

**Mr. G. S. Hartley** (*London*) expressed his appreciation of Professor Kruyt's having focussed attention so clearly on the two different methods of approach to the electrical properties of colloidal particles—the extrapolation downwards from the properties of matter in bulk and the extrapolation upwards from individual ions. No one could doubt that the two routes, if both could be correctly followed, must lead to the same result. Professor Kruyt preferred the former on the grounds that our knowledge of the latter was too slight, being confined

* On the four preceding papers.

to the behaviour of small ions of low valence. The speaker said that, without wishing to make light of the difficulties in the latter method, he thought that Professor Kruyt had failed to draw attention to a difficulty in the former which seemed to him very great and of fundamental importance.

In extrapolating from the macro-wall downwards we make use of a certain potential function, the $\zeta$-potential, and, since most of the properties in which we are interested can be expressed in terms of it, we are not greatly concerned about the difficulty of relating the charge of the particle with this function. The advantage of the $\zeta$-potential which enables us to make use of it for the desired extrapolation is that it can, for most lyophobic colloids, be assumed independent of the size of the particle. Now this assumption can only be made if the material of the particle remains *in the same physical state* as its size is reduced. In the case of many of the substances which we are accustomed to call colloidal electrolytes this is certainly not true. To take one example : the micelle-forming long-chain salts have a well-defined solubility in water : at the saturation concentration the chemical potential of the salt in the crystalline solid is equal to that in the micellar condition in solution : at concentrations below this the former is obviously the greater : the physical state of aggregation in the micelle is therefore different from that in the solid and it is therefore dangerous to assume that any $\zeta$-potential determined by observation on the solid is of any significance for the behaviour of the micelle. While agreeing with Professor Kruyt that the difficulties in the way of an extension of simple electrolyte ideas to the micellar case were great and at present not surmounted, the speaker thought that the difficulties in the way of extrapolation from the macro-wall downwards in the case of such substances as soaps and dyes was insurmountable, *because a macro-wall in the same physical state as the surface of the micelle could not be obtained.*

Such substances, however, owe their charge to the dissociation of ionogenic groups which are chemically inseparable from the bulk of the particle. It is therefore possible to calculate the charge of the particle from its mass or volume, if the problem of the degree of dissociation of the ionogenic groups can be solved, *because there is a necessary stoichiometric equivalence between mass and maximum possible charge.* In the interpretation of the various measurements which could be made on these substances, the further problem of the distribution of the ions in the double layer or atmosphere had to be attacked. Of the peculiar difficulties of this latter problem the speaker said he was well aware, having discussed them in his own paper, but he wished to point out that they were just as much obstacles to the calculation of the charge from the $\zeta$-potential and it was important to appreciate that the advantage of the $\zeta$-potential method, where applicable, was not that this problem was made easier, but that its solution was in many respects unnecessary.

It was interesting to note that where the $\zeta$-potential method was applicable, *i.e.*, where the material of the particles was in the same physical state in the ultra-micro-particle and the macro-solid, there could be no true thermodynamic equilibrium with regard to this material among the particles of various sizes, so that if the sol were indefinitely stable it could only be because the rate of attainment of equilibrium was indefinitely slow, this being so because the difference of chemical potential between the particles was very small (*i.e.*, the

particles still very large in terms of molecular dimensions) or because
the material was very insoluble in the molecular disperse condition and
the electrical repulsion prevented adhesion of the particles. Colloidal
particles could only exist in true thermodynamic equilibrium if the
material constituting them was in a different physical state from that
in the macro-solid. This was in practice true only for those colloids
the charge of whose particles was chemically inseparable from their bulk.
Charged colloids therefore divided themselves into two fairly well-
defined classes—on the one hand a class where the bulk of the particle
is made up of insoluble material in regard to which there is no equilibrium,
and whose charge is due chiefly to preferential adsorption of foreign
ions : to this class the $\zeta$-potential treatment is applicable but the charge
not stoichiometrically related to the mass of the particle—and on the
other hand a class in which the particle is made up of a definite ionising
compound with regard to which there is true equilibrium and whose
charge is due to ionisation of this compound : to this class the $\zeta$-potential
treatment is not applicable, but the charge is stoichiometrically related
to the mass of the particle : the particles of this class are usually very
much smaller than those of the first (a difference emphasised by
Freundlich). The speaker would prefer (with McBain and others)
to confine the term " colloidal electrolytes " to this latter class, though
admittedly on grounds of convenience rather than of etymology.

**Dr. E. Valkó** (*Ludwigshafen a. Rh*) said : In the discussion, Professor
Kruyt raised the question whether the assumption of the ionic structure
of the double layer is necessary for the explanation of the $\zeta$-potential. It
is true that Helmholtz constructed his theory before the foundation of
Arrhenius theory. But this was a defect of birth of his brilliant double
layer theory, as clearly proved in an excellent paper by McBain and Mrs.
Laing-McBain.[1] Already Smoluchowski[2] had expressed the opinion
that progress in the theory of electro-osmotic phenomena is only possible
by application of the theory of ions. Indeed, our present knowledge of
the structure of matter does not allow us to assume any other mechanism
for the transport of matter by electric current than the transport of
free ions. Dipoles alone can only be oriented, but not moved, by electric
currents. If we renounce the assumption of the ionic structure of the
double layer, we renounce any possibility of explaining the electrokinetic
phenomena, at least for the moment.

The problem of the origin of the electric charge at the paraffin/water
surface is difficult, but I feel sure that the theory of the ionogenic surface
compounds will, in this case also, prove true. We can use as a working
hypothesis the assumption that there are fatty acids with large mole-
cular weight fixed at the surface which are the carriers of charge. Since
they are insoluble in water, they will not be separated from the paraffin
mixture by the ordinary purification methods. An amount which is
too small to be analytically demonstrable is sufficient to cause the
observed streaming potential. This assumption can be tested by
application of indirect methods analogous to those used by Pauli.

**Dr. F. L. Usher** (*Leeds*) said : Professor Kruyt's treatment, in which
a very small area of the surface of a spherical particle is considered as
a plane surface with a diffuse double layer, raises the interesting question
of the possible influence of curvature on the electrical conditions at the
interface, since with extremely small particles of equivalent radius

[1] McBain and M. E. Laing-McBain, *Z. physik. Chem.*, **161**A, 279, 1932.
[2] v. Smoluchowski, *Handbuch der Elektrizität*, **2**, 425 (Stuttgart) 1914.

1-5 m$\mu$, even 1 square micron of surface has substantial curvature. Two lines of evidence indicate that either the $\zeta$-potential or the surface density of charge on particles in sols increases as their size decreases. First, so far as is known, the mobility of particles of the same material immersed in the same intermicellar liquid does not vary much with size, whereas according to Henry's analysis the mobility of extremely small particles should be greatly reduced if the surface density of electrification remains constant. Secondly, experiments by Thiessen and others have shown that the stability of gold sols towards electrolytes increases with decreasing size. A similar assumption seems capable of explaining an interesting phenomenon which has recently come to light. The concentrations of potassium, sodium, and lithium ions needed to reduce the potential (or charge) of particles in a gold sol to a given fraction of the initial value are about the same when the radius is greater than 18 m$\mu$. When, however, the radius is 1-3 m$\mu$, between 4 and 5 times as much lithium as potassium is required. Thus sufficiently small particles of a lyophobic substance tend to behave towards these ions as though they were lyophilic, although the explanation may be different in the two cases. In the case of the gold sols I would suggest that the smallest particles have a higher surface density of charge, and that in consequence a greater number of alkali metal ions have to approach each unit area of surface in order to effect a given reduction than with larger particles. If this is so, the greater size of the hydrated lithium ions may lead in the former case to a " crowding " effect which would not be observed with large particles, so that a higher bulk concentration is needed to produce the required result.

**Professor A. Frumkin** (*Moscow*) said : Professor Kruyt has pointed out that colloidal problems can be attacked from the point of view either of the double layer theory or of the theory of solutions. It appears to me that in applying the double layer theory we must be careful not to push too far the idealisation of the structure of the surface layer. When discussing the relation between the stability of a metal sol and the existence of a double layer on the surface of its particles, colloid chemists refer as a rule to a schematic picture, assuming that there is nothing on the surface of the particles except electric charges of one sign on the metal and of ions of opposite sign, distributed in the solution to a certain depth.

At the present moment it would be difficult to decide the question, whether the existence of a double layer of that kind is sufficient, by itself, to stabilise the sol, since the structure of the surface in most systems which have been hitherto investigated is undoubtedly more complicated. Let us take as an example the surface of a platinum electrode in hydrochloric acid.[3] The relation between the quantity of electricity $\theta$ necessary to charge the electrode to a certain potential $\phi$ is given by the curve drawn on Fig. 1. If we start with the reversible hydrogen potential A, there is first a region of very low capacity AB, where the electrode is covered by a surface hydride or a layer of bound atomic hydrogen. A part of it is ionised and thus causes a negative charge of the surface. In the BC region there is only a normal double layer with positive charges on the platinum surface. In the CD region the surface is covered by an oxide or by more complex compounds containing oxygen and the anion of the acid. The correctness of this picture can be demonstrated by a combination of polarisation measurements with

[3] Frumkin and Šlygin, *C.R. Acad. Sc., U.R.S.S.*, **2**, 176, 1934.

adsorption data, as has been discussed elsewhere. The surface of or-
dinary platinum sols is in a state corresponding to the CD region of the
curve. Whether a stable sol with particles carrying only a normal
double layer (as in the BC region) can exist is not known ; it would be
certainly very important to decide this question. N. Bach and N.
Balashewa (*Karpow Chemical Institute*) succeeded recently in preparing
platinum sols, which correspond to a point of the AB region of the curve.
They used the ordinary Bredig method, except that the disintegration
of the platinum was carried out in water saturated with hydrogen and
after the disintegration hydrogen was bubbled through the solution for
a certain time. Adsorption measurements on platinum electrodes show
that under these conditions surface oxides should be reduced and a
hydride surface obtained. The sols are negatively charged (cataphoretic
measurements) through partial ionisation of the surface hydride and
appear to be fairly stable ; which is rather unexpected from the point
of view of the Pauli theory. Their conductivity is practically that of
the original water, *i.e.*, $0.5 \times 10^{-6}$. It is probable that the formation
of the surface hydride is of great importance in the stabilisation of these
sols. Adsorption measurements carried out recently by Bruns and
Ablesowa [4] have shown that the van der Waals' field of force at the
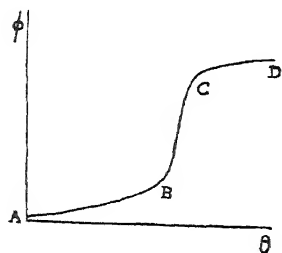


FIG. 1.

surface of platinum (as judged by its ad-
sorptive power towards ethylene) is enor-
mously decreased through the formation of
surface hydride. We may safely assume
that in a similar way the saturation with
hydrogen of the free valencies on the sur-
face of the platinum particles decreases the
attractive forces between two particles and
thus helps to stabilise the sol. It is thus
impossible to decide from these experiments
whether the existence of a double layer
would be sufficient to stabilise the sol in
the absence of any other stabilising factors. The question could be
solved by preparing platinum sols whose surface conditions would corre-
spond to the BC region, but so far our attempts in this direction have
not been successful. However, platinised charcoal saturated with hydro-
gen gives very stable suspensions and, in this case, it appears that the
formation of a normal double layer is the only stabilising factor which
has to be taken into account.[5]

Comparing the double layer scheme with the picture of surface
compound formation, as given by Pauli, we must bear in mind that
the normal structure of the double layer is often complicated by the
specific adsorption of anions.[6] The distribution of charges which exists
in the double layer in that case is, in many respects, very similar to that
assumed by Pauli.

The stabilising action of electric charges on metal sols is usually
connected with the $\zeta$-potential, but a non-diffuse double layer, which
would not give any $\zeta$-potential must still exert a stabilising action,
increasing the binding energy between the particle and the solvent.
This is shown, for instance, by the fact that the metals are much better

[4] Bruns and Ablesowa, *Acta physicochimica, U.R.S.S.*, 1, 90, 1934.
[5] N. Bach, *Koll. Z.*, 64, 153, 1933 ; Pilojan, Kriworutschko and N. Bach,
*ibid.*, p. 287.
[6] Frumkin, *Physik. Z. Sowjetunion* 4, 253-259, 1933.

wetted by water at strong polarisations. [7] This effect is a function of the total potential difference and independent of the $\zeta$-potential. The existence could perhaps explain the differences in the stabilising action of ions which give rise to the same electro-kinetic charge mentioned by Professor Kruyt.

There remains but one fact which I should like to point out. All theories of the double layer which have been developed up to now consider the planes parallel to the solution/metal interface as equipotential planes, *i.e.*, they assume that the lines of force are at a right angle to the metal surface. The real distribution of the lines of force must be more or less as shown by Fig. 2 and, especially in the case of polyvalent ions, the properties of the double layer might be very different from those which we should expect on the basis of the idealised theory.[8]

**Dr. Karl Söllner** (*London*) said : As to the remark of Professor Kruyt about the electrokinetic properties of paraffin and similar substances I would like to point out, with all necessary reserve, that I am rather doubtful, whether we are dealing always in those cases really with the interface water-paraffin or whether gases, most likely in the form of small lenses or layers, play an important rôle. Experiments[9] have shown the great influence of gases upon the formation of emulsions by means of shaking or by applying ultra-sonic waves. In many cases it is quite impossible to obtain emulsions of pure substances in the absence of gases whereas in their presence emulsions are easily formed ; in other cases emulsions formed in the presence of gases are much more stable than those obtained in the absence of gas. As far as we can judge now it seems likely, therefore, that gases favour not only the formation but also the stability of emulsions. As mentioned above we think, that this can be explained by the assumption of layers of gas or gas lenses. This phenomenon may be much more common than we know at present.[10] Investigations in this direction are in progress.
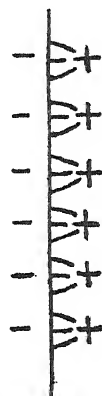


FIG. 2.

**Professor H. R. Kruyt** (*Utrecht*) said : In the short survey of my paper I mentioned that colloids are polymolecular particles ; if not, the word colloid has hardly any sense. To Dr. Bigwood's question whether a *large molecule* is not already a colloid, I should like to state this : Nobody pretends that the colloidal particle of a gold sol, an $As_2S_3$-, a $AgI$-, a mastic-sol or an oil emulsion consists of one molecule. With dyestuffs and soaps, where we know exactly the molecular weight, the colloidal properties are ascribed to polymolecular or polyionic aggregations. It is only with proteins and similar compounds, where the chemical molecular weight is dubious, that monomolecular colloidal particles are assumed. This seems arbitrary, the more since we know that mere dehydration of these hydrophilic colloids changes them in hydrophobic ones, which behave exactly as those mentioned above. And as the behaviour of gold sols, etc., can be understood completely by the assumption

[7] Kabanow and Frumkin, Z. *physik. Chem.*, **165A**, 433, 1933; Kabanow, *Koll. Z.*, **65**, 101, 1933.

[8] *Physik. Zeitschr. Sowjetunion*, loc. cit., p. 257.

[9] Rogowski and Söllner, *Z. physik. Chem.*, **157**, 1933.

[10] W. Spring, *Ann. Soc. Geol. Belg.*, **28**, 1901 ; **29**, 1902 ; *Bull. Soc. Belg. Geol.*, **17**, 1903 ; *Bull. Acad. Belg.*, **37**, 790, 1899.

of an electric double layer at a polymolecular wall, there seems to be no reason to look upon the hydrophilic particles in a different way.

I accept with full approval Dr. Hartley's graphical representation on the extrapolation of the Debye-Hückel theory to colloids. Moreover, the valency of an ion does not characterise its behaviour entirely : the distance between the charges plays an important rôle,[11] but it is not easy to account for this quantitativety. When studying the influence of neutral salts on the shifting of the $p_H$ with gelatine sols one of my students[12] found that gelatin behaved like a monovalent electrolyte.

When I spoke of two types of $\zeta$ potentials I had this in mind : the origin of the double layer, as I mentioned in my paper, may be ascribed either to ions of the material of the wall or to ions, preferentially adsorbed by that wall. The streaming potentials of water pressed through a paraffin tube are very high.[13] An AgBr-capillary shows a potential (the wall being negative) at concentrations of $AgNO_3$, where no doubt the charge of the Br-ions at the periphery (i.e., on the edges of the particle) is compensated.[14] What ions constitute the double layer at paraffin and at the faces of silver halogenide particles ? The only explanation would be : adsorbed OH-ions ; but this seems not to be probable, as in that case the H-ion would have a very special influence, as it has a special influence on the concentration of the OH-ions. However, there is hardly any difference between a K- and an H-ion on this $\zeta$ potential. Moreover, it is interesting that colloidal stability with silver-halogenides is due only to the potential, induced by a double layer of the normal type, originating from ions that determine the total electric potential (viz. halide-ions).

The problem arises whether such a $\zeta$ potential of the second type is really due to an ionic double layer. The Helmholtz' theory is older than the theory of electrolytic dissociation. However it is difficult to give a satisfactory explanation nowadays, I have thought of orientated water dipoles, but I must acknowledge that this is not clear. Unpolarisable liquids give however no electric kinetic phenomena.

In his introductory paper Freundlich mentions as a special characteristic of colloidal electrolytes their spontaneously going into solution. I wonder whether this must be ascribed directly to a difference in the electric character of the particles or to a difference in solvation. I should not like to emphasise that there is no relation between electric properties and solvation, but it seems to me that the antagonism " ionic micelle or electric double layer " is not analogous to that of " spontaneous dissolution and peptisation by a third component " ; it seems that the former is much closer related to " sufficient and insufficient solvation."

In reply to Dr. Söllner : The problem remains the same, whether we have a paraffin-water or an air-water surface, both being themselves absolutely incapable to produce ions.

**Mr. G. S. Hartley** (*London*) said : Although *as far as the equilibrium properties are concerned* the effect of increasing particle size acts in the reverse direction to the effect of increasing charge and consequently a colloidal electrolyte may, over a limited concentration range, show some resemblance to a uni-uni-valent electrolyte, this will certainly not be true of the *mobility of the particle*. Here, increasing size and increasing

[11] See H. S. Simms, *J. physic. Chem.*, **32**, 1121, 1928.

[12] A. H. W. Aten, Jr., unpublished.

[13] See P. Julien, *Diss.*, Utrecht, 1933, and Ruyssen and Kruyt, *Proc. Roy. Acad. Science, Amsterdam*, 1934.

[14] Where the *Ladungsnullpunkt* is attained ; see Verwey's and my papers in *Z. physik. Chem.*, **167**, 1933-34.

charge act together to increase the braking effect of the atmosphere. No similarity to a univalent ion would be found if the change in the mobility of the gelatin ion with concentration of gelatin or salt were measured.

**Dr. A. Wassermann** (*London*) said : Gross and Halpern [15] and Bjerrum [16] treated the theory of a heat effect in a dielectric medium, and have arrived at a relation between the heat of dilution of an ionic-solution and the electric energy change according to Debye and Hückel.

Nernst [17] and Naudé [18] and Lange [19] and co-workers have measured in the differential-calorimeter the heat of dilution of extremely dilute electrolytes (heat-effects 0·02-2 g.-cal./10 cm.$^3$), and have discussed the degree of dissociation of these electrolytes on the basis of the calculations of Gross, Halpern, and Bjerrum.

In any attempt to apply the Debye-Hückel theory to simple colloidal electrolytes, the degree of dissociation of the colloidal electrolytes and therefore their heat of dilution is of great interest. Changes of the degree of aggregation during the dilution, and other complicating factors, will have to be considered.

**Dr. F. Eirich** (*Wien*) said : With regard to Dr. Hartley's paper may I call attention to the fact that, in addition to tungstic acid sol, many other colloid acids, *e.g.*, purified gum arabic, gum tragacanth, silicic acid, arsenic sulphide and platinum sol yield curves on conducto-metric titration, which clearly show the presence of different acid stages. These colloid acids react on neutralisation like crystalloid acids and are similar to these, which are considered as the charging compounds. Thus the anions on the particle surface do not always combine with a poly-valent ion,* but they frequently retain some part of their individual qualities. Consequently it sometimes seems more suitable to consider a colloidal electrolyte as a solution, in which one kind of the ions is not evenly divided, but is found localised in little spots, whereby the concentration of those ions is determined by their distance from each other on the particle. Probably the same division of the *Gegenions* will arise, if one visualises the particle surface as that of a polyvalent ion or as a residue of a certain kind of ions.

**Professor Wo. Ostwald** (*Leipzig*) said : Dr. Henry of Manchester published some years ago a very interesting development of the theory of the electrical double layer, which has not been mentioned in our discussion so far. In this theory Henry applies the fundamental con-ceptions of the Debye-Hückel theory of electrolytes itself to develop the structure and the properties of the double layer of any surfaces, *e.g.*, also of macroscopical ones. We find here a very interesting bridge between the theoretical treatment of highly dispersed charged particles such as common ions and micro- or macroscopical charged surfaces, and a very general way to consider both from the same point of view.

**Dr. Ph. Gross** (*Wien*) said : I agree with Professor Kruyt and Dr. Hartley in saying that generally speaking one should not apply the principle of ionic strength to colloidal electrolytes. In certain cases, however, it may be useful to describe the state of solutions of colloidal electrolytes by comparing them with real strong electrolytes in a manner which I now should like to discuss.

[15] *Physik. Z.*, **26**, 403, 1925.
[16] *Z. physik. Chem.*, **119**, 145, 1926 ; *Trans. Faraday. Soc.*, **23**, 445, 1927. *Cf.* also Lange and Meixner, *Physik. Z.*, **30**, 670, 1929.
[17] *Z. physik. Chem.*, **135**, 237, 1928.　　　　　[18] *Ibid.*, **135**, 209, 1928.
[19] *Fortschritte Chemie, Physik., physik. Chem.*, Bd. 19, Heft 6.
* The theory of adsorption does not allow a gradual neutralisation.

3 *

As an example of a colloidal electrolyte I choose an aqueous sodium hydrosilicate (NaHSiO$_3$) solution. The measurements of the depression of freezing-points and of the conductivity I use here are taken from various authors.
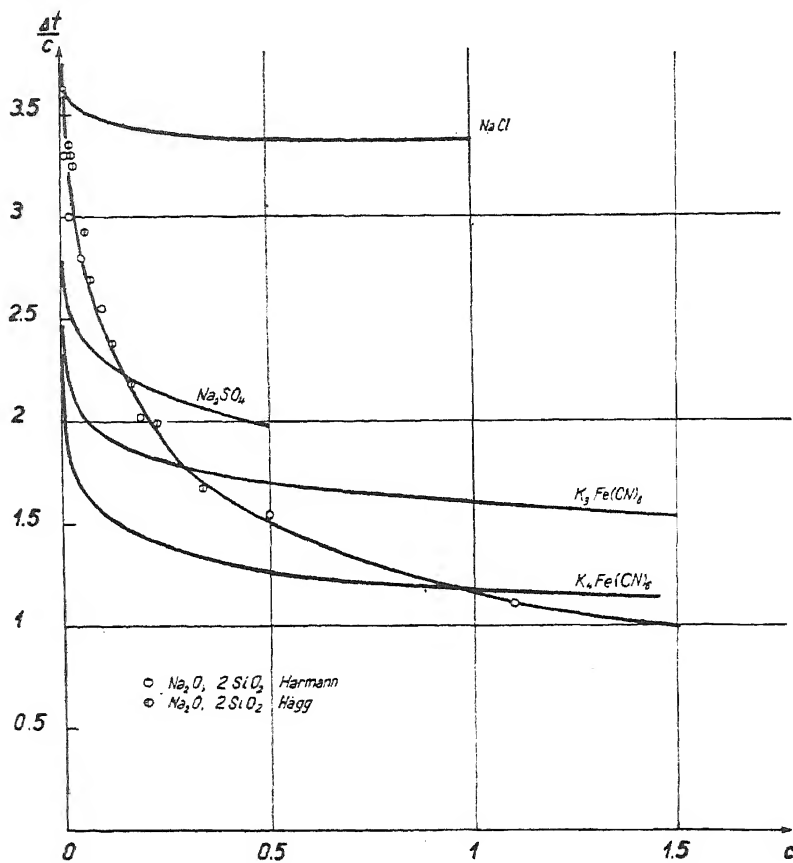


FIG. 1. $c =$ Equivalents/Litre.

Fig. 1 shows the curves if the molecular freezing-point depression $\left(\dfrac{\Delta t}{c}\right)$ is plotted against the concentration $(c)$:

(1) of a uni-univalent electrolyte, sodium chloride (NaCl),
(2) of a uni-divalent electrolyte, sodium sulphate (Na$_2$SO$_4$),
(3) of a uni-trivalent electrolyte, potassium ferricyanide (K$_3$Fe(CN)$_6$),
(4) of a uni-tetravalent electrolyte, potassium ferrocyanide (K$_4$Fe(CN)$_6$),
(5) of a sodium hydrosilicate solution (NaHSiO$_3$).

We see that the curve of NaHSiO$_3$ cuts the other four curves at different concentrations. We may assume that the association of the HSiO$_3^{\bullet}$ ions leads to colloidal particles which have, at those concentrations, the same electrical charges as the ions of the respective electrolyte. The degree of association thus obtained is, of course, a rather rough mean value.

In doing the same with measurements of conductivity there arises a certain difficulty. We cannot state with any certainty the various mobilities of the different colloidal particles. I have for the moment neglected this difficulty, which I think will have to be overcome by a more thorough treatment.

In Fig. 2 the coefficient of conductivity ($f$) of strong electrolytes of the different valency types and of $NaHSiO_3$ is plotted against the concentration ($c$). We find that the points of intersection of the $NaHSiO_3$ curve with the other curves are found within the same range of concentrations as in the first picture (Fig. 1) respectively.
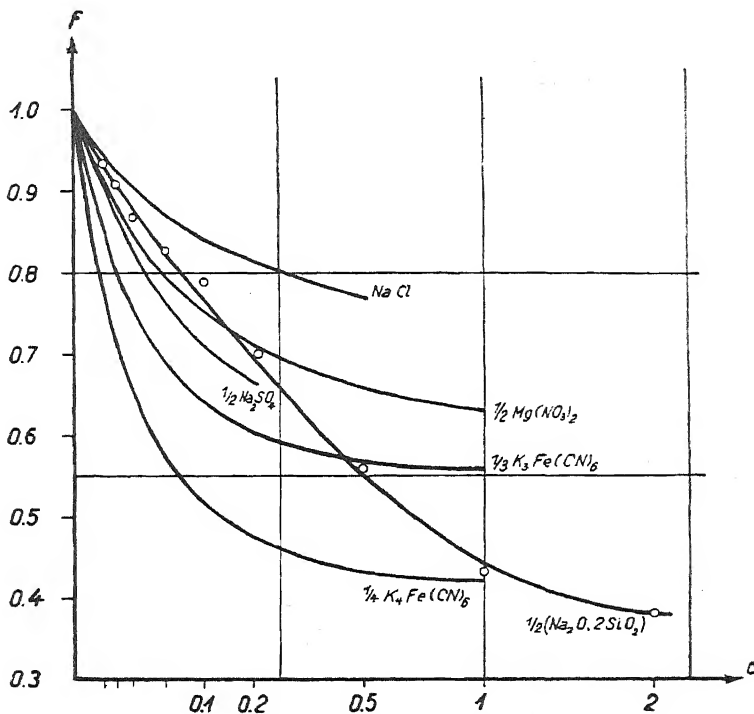


FIG. 2.   $c$ = Equivalents/Litre.

The whole method, of course, needs a little more justification. To this end, for instance, measurements of the activity coefficient of the sodium ion would be very useful.

**Dr. Conmar Robinson** (*London*) said : Professor Rabinovitch points out the difficulties met with in attempting to apply a theory of colloid electrolytes to lyophobic colloids, as is done by Pauli. Nevertheless he concludes, in the last paragraph of the summary of his paper, that it is desirable to build up such a theory (" but attempts have to be made to build it up ").

If by applying a theory of colloidal electrolytes to lyophobic colloids he means explaining all the properties of lyophobic colloids by methods analogous to those used to explain the properties of colloidal electrolytes such as soaps, dyes and proteins, I feel he is here suggesting that we attempt the impossible. There is a difference between these two classes

of colloids which is more fundamental than any of the differences which have been stressed by Professor Rabinovitch. This difference has already been mentioned by Professor Freundlich in his introduction and is as follows : On the one hand we have dyes, soaps and proteins, substances which dissociate into ions or ion aggregates on being dissolved—here all the substance is determining the colloidal properties —and on the other hand colloids such as gold sols which possess a central core which plays no direct part in many of the colloidal properties of the solution, these colloidal properties being to a very large extent determined by small amounts of " foreign " electrolytes, which are bound to the core of (*e.g.*) gold. All the colloidal properties of both these classes will never be explained by the same theories. But in solving a particular problem it may be useful to treat any charged colloid as a colloidal electrolyte. For instance, this was done by Mr. Hartley and myself [20] in explaining the high diffusion of starch obtained by Bruins. A similar treatment could have been used to explain the diffusion coefficient of any charged colloid, but it does not follow that because we used such a treatment we necessarily consider starch to be a colloidal electrolyte or that all its colloidal properties can be explained by an extrapolation of our knowledge of ordinary electrolytes.

**Professor A. J. Rabinovitch,** in reply, said : I completely agree with Mr. C. Robinson that there are serious doubts as to the possibility of constructing a full theory of colloidal electrolytes capable of explaining the behaviour of lyophobic colloids. I think that in this respect the colloids may be divided into two different classes, in accordance with Freundlich's classification, only a part of lyophilic colloids being typical colloidal electrolytes.

However, attempts may be made to build up a general theory, treating all the colloids from one point of view, as has been done in the interesting paper by Hartley. Unfortunately, any theory of electrolytes as applied to lyophobic colloids is very difficult to verify experimentally on real colloidal systems, the colloidal part of the system playing a very small rôle in comparison with the electrolyte contents.

**Dr. E. Valkó** (*Ludwigshafen a/Rh.*) said : I should like to discuss some points in the interesting paper of Professor Rabinovitch, in the name of Professor Pauli and myself.

Professor Rabinovitch quoted our answer to Mukherjee. In this we referred to the well-known chapter in the history of the electrochemistry of colloids where, on the basis of misinterpretation or of erroneous methods, research workers were mislead to assume that the fundamental laws of solutions are not applicable to these systems.

The one case was the interpretation of the osmotic behaviour of proteins. Here the influence of membrane potential was not taken into account. The other case was the measurement of steam tension and of the boiling-point of soap solutions with the aid of an insufficient method.

In the first case the theory established by Donnan, in the second case the new exact measurements carried out by McBain, showed that the denial of the fundamental principles was hasty. Our answer to Mukherjee contained also, however, a series of detailed arguments against his conclusions.

Professor Rabinovitch doubts whether potentiometric measurement can give a value for the activity of the *Gegenions*. His criticism of the

work of Pauli and co-workers fails, however, just as his criticism of the work of Wiegner and Pallmann. His picture of the ideal colloid ignores completely the fact that the electric double layer is, even on the motion-less surface, diffuse and not rigid. Our ideal colloid solution has the following properties :—

(1) It is diluted.
(2) The charge density or electric potential on the surface of the colloid particle is small.

In such a system all the *Gegenions* are free and therefore the activity coefficient is equal to unity. The potentiometric measurement gives the value for the concentration of the *Gegenions*.

In the real colloid system these conditions are not fulfilled. There-fore the activity coefficient is smaller than unity. The potentiometric effect of the *Gegenions* is less than their concentration. Since Pauli (as well as Wiegner) based his work on this assumption, his interpretations are perfectly sound and correct. The situation is just the same as in the solutions of ordinary electrolytes.

Finally, I cannot agree with Professor Rabinovitch's view that the fact has generally been neglected that the charging ions are, in regard to the likelihood of combination, in equilibrium with the surface of colloid particles. Pauli and I have dealt with this equilibrium in detail. Only in those systems which are thoroughly purified, preferably by electro-dialysis, is this equilibrium so established that the fraction of free charging ions is comparatively small. With the electric current the free ions must be driven out. In other systems the free-charging ions were carefully taken into account by us.

**Professor A. J. Rabinovitch,** in reply, said : Dr. Valkó has not pointed to the considerations of other authors as to the equilibrium of ions between the particles and the intermicellar liquid in order to em-phasise the particular importance which the present authors ascribe to this factor.

With regard to the second point of Dr. Valkó's criticism, there is a profound discrepancy between the views of the school of Pauli and that of the author, and no agreement can be attained on this point at present. We still believe that our point of view has been sufficiently clearly exposed in the thermodynamical argument in our paper (p. 5), and no serious objections have been raised against it.

**Dr. H. Neurath** (*Wien*) said : In his paper Professor Rabinovitch calls attention to the fact that the determination of the $p_H$ in iron-oxide sols, by means of the hydrogen electrode, as carried out by Pauli and Matula,[21] leads to wrong results, owing to the poisoning of the electrode by Fe ions. Hence all calculations of the charge (*Kolloidaequivalent*) are inexact.

I desire to point out that these authors, at the time, realised these difficulties, and therefore they compared the measurements of the $p_H$ in the sol with those in the filtrate flocculated with potassium chloride. Both measurements agreed almost exactly. As it was shown in later papers, [22],[23] the activity of hydrogen ions in iron oxide sols can be deter-mined exactly, if the sol is set free from iron ions by thorough electro-dialysis. We can ignore, however, all these doubts if we deal, for

[21] W. Pauli and J. Matula, *Koll. Z.*, **21**, 49, 1917.
[22] Winnifred L. McClatchie, *J. physical Chem.*, **36**, 2087, 1932.
[23] H. Neurath and W. Pauli, *Z. physik. Chemie*, **163**, 351, 1933.

example, with an aluminium oxide- or a thorium oxide sol, [24], [25], [26] with which the possibility of an oxidation-reduction potential is excluded.

I wish to emphasise that all these investigations are carried out with sols, of which the concentration and the activity of all types of ions were exactly known.

**Professor A. J. Rabinovitch,** in reply, said : Our measurements of $p_H$-values of ferric oxide sols made with different electrodes (Pt-$H_2$, quinhydrone, glass electrode) have decidedly shown that the $Fe_2O_3$-sols are acid.   This could not be stated by Pauli and Matula because the Pt-$H_2$-electrode is poisoned in ferric oxide colloidal solutions.

It is easy to understand that Pauli and Matula found very high $p_H$-values (near to neutrality) in the filtrates after coagulation of ferric oxide sols by electrolytes or in corresponding ultrafiltrates.   As previously found by the authors, electrolyte coagulation is accompanied in this case by an increase of $p_H$-values, owing to the change of hydrolysis conditions.   If the filtrate after coagulation was nearly neutral, the sol itself must have been acid.

**Dr. E. Valkó** (*Ludwigshafen a/Rh.*) said : In connection with the very interesting remarks by Professor Frumkin, I should like to stress the fact, that the difficulties in applying the theory of the diffuse double layer especially to the question of the capacity are often due rather to the inner component of the double layer than to its outer diffuse part. Only the latter is the object of the theory of Gouy and of Debye-Hückel. I have the impression that the complications in the structure of the double layer lie chiefly in the composition of the inner part.   It is a question of the formation of complex compounds at the surfaces, the nature of which is in many cases recognised by Pauli.

**Dr. F. Eirich** (*Wien*) said :   Professor Rabinovitch emphasised some consequences of his reflections on coagulation.   But the two possibilities of the coagulation described are not sufficient to explain a great deal of important experimental work.   I will only give one characteristic example : which is already contained in Pauli's paper. I refer to the flocculation results of very well-defined gold sols, prepared by electrical dispersion in purest diluted hydrochloric acid or sodium hydroxide.   If to these acid sols a caustic is added (or vice versa to the alkaline sol an acid) they show a peculiar behaviour.   Their stability is gradually diminished as they are more and more neutralised, then flocculation occurs at a still very small concentration and later, on greater additions of HCl or HBr only a new range of stability follows' leading to a new flocculation at high concentration.   Any coagulation theory assuming a building of insoluble compounds or specific adsorption is too schematic to explain either our irregular and irreversible flocculation series and, at the same time, the still more remarkable difference between the effects of different kinds of acid, which difference disappears (in the presence of the anions known to form complexes with gold. All these facts can, however, be well explained from the electrochemical point of view as an exchange of chlorine with hydroxyl ion in the interior of the complexes on the surface of the gold particles, which causes coagulation or electrical charge.   Therefore these variations and complications seem to be more readily explained chemically by means of the well-known ionic or complexionic reactions, without any assumption of special adsorption.

[24] W. Pauli and E. Schmidt, *Z. physik. Chemie*, **129**, 199, 1927.
[25] F. Muttoné and W. Pauli, *Koll. Z.*, **57**, 312, 1931.
[26] W. Pauli and A. Peters, *Z. physik. Chemie*, **135**, 1, 1928.

**Professor A. J. Rabinovitch** said, in reply : It is quite probable that we have not enumerated in our paper all the possible cases of coagulation. This was not our purpose. A full theory of this process does not exist at the present time.

Anyhow, there is not a very great discrepancy between our views in the case cited by Dr. Eirich. He emphasises the importance of processes in the inner part of the double layer, treating them from a chemical point of view. In our paper we also emphasise the importance of the inner part of the double layer, in considering the adsorption of *both* ions of the stabilising electrolyte, *i.e.*, of *Nebenionen*.

**Professor Wo. Ostwald** (*partly communicated*) : The discussion between Professor Kruyt and Mr. Hartley as to whether colloids with electrical conductivity are better treated from the standpoint of electrical surface phenomena or from the standpoint of the ionic theory is a partial resurrection of the discussion held thirty years ago on the question, whether colloids are better treated as heterogeneous or as homogeneous systems. The latter question is hardly discussed any more now. The introduction of the conception of " dispersed systems," including macroscopic suspensions as well as molecular dispersed solutions, closed this discussion. This conception meant an outspoken and conscientious *emancipation* from the classical ideas of heterogeneous and homogeneous systems, based upon the fact (to quote J. Perrin) that " even the most fruitful scientific conceptions lose their fruitfulness and even their meaning if they are applied to phenomena which lie outside the experimental field for which these conceptions have originally been made for." Colloid particles are not phases according to Gibbs' own definition, because the amount of energy and entropy located in their surfaces is *not* to be neglected when compared with the amount of energy and entropy located in the interior of the particle. Nor do gold sols, for example, obey the laws of Faraday for normal ions, the masses transferred in cataphoresis not being proportional to the number of elementary charges, and the masses not being in equivalent proportions to each other, if different sols are compared. Of course it seems *a priori* possible, empirically as well as theoretically, to extrapolate from both points of views, as Mr. Hartley points out. This has been tried over and over again. But the overwhelming evidence goes to show firstly that the experimental transition-curves very frequently show maxima or minima in the region of colloidal dimensions, so that extrapolation is somewhat dangerous ; and secondly, that enlargements or modifications of the classical theories for colloidal systems tend to become extraordinary complicated and correspondingly diffuse. Instances are at hand.

The safest way seems to treat colloidal systems—generally as well as in regard to their electro-chemistry—as essentially *new* systems. It is an error to believe that the phenomenological or functional stage of colloid science can be passed over or that it is already finished. We do not even know, for instance, the general shape of such a simple function as conductivity—dilution for the different types of conducting colloids, and Mr. Robinson's graph of this function for benzo-purpurine is a very pretty instance of this colloidal specificity shown even by a colloid that is very closely related to common electrolytes. This point of view, the theoretically unbiassed collection and description first of the fundamental experimental functions in colloids, is what is indicated by the use of the word " *Eigengesetzlichkeiten* " of colloids by Mukherjee and by myself. You may call this point of view a very modest one. We think modesty in this case to be especially progressive.

**Dr. Ph. Gross** (*Wien*) said : In connection with one of the remarks of Professor Kruyt I would refer to a paper by Scatchard and Kirkwood.* This paper deals theoretically with the interaction between common ions and ions, the charged groups of which are widely separated from each other. The problem is treated according to outlines quite similar to the treatment originated by Debye and Hückel, but the results are rather different.

**Dr. F. Fairbrother** (*Manchester*) said : There exists a potential between the solid and liquid phases of a melting solid or a freezing liquid. This was first observed by Faraday [27] in the case of ice and water, and has also been shown to exist in the case of a number of organic compounds.[28] It is difficult to imagine an ordinary ionogenic mechanism in these circumstances.

**Dr. A. H. Hughes** (*Cambridge*) said : A possible source of the high negative electrokinetic potential obtained with paraffins against water is the presence of minute traces of long-chain fatty acids. A quantity of such material as small as $10^{-7}$ gm. per sq. cm. present as an oriented monolayer at an oil-water interface may produce a potential difference due to partially ionised carboxyl groups of from 2-300 millivolts.

**Professor W. C. M. Lewis** (*Liverpool*) recalled the findings of E. Jones [29] in connection with the effect of vigorous stirring upon the magnitude of the $\zeta$ potential difference. If the colloidal particles (gold sol) have had their $\zeta$ value reduced to zero by suitable addition of electrolyte, the effect of stirring is to hasten the rate of aggregation of the individual particles as one would expect purely on a collision frequency basis. On the other hand, if the electrolyte concentration is insufficient to reduce $\zeta$ to zero, the effect of stirring is actually to slow down the rate of aggregation. This can be explained on the basis of a mobile outer portion in the double layer, the removal of which effectively increases $\zeta$. The results seem therefore to demand the actual existence of a double layer, of the Gouy-Stern type in general.

* G. Scatchard and J. G. Kirkwood, *Physik. Z.*, **33**, 297, 1932, see also J. G. Kirkwood, *J. Chem. Physics*, **2**, 351, 1934.
[27] Faraday, *Experimental Researches*, **2**, No. 2131, 122.
[28] Fairbrother and Wormwell, *J. Chem. Soc.*, 1991, 1928.
[29] *Trans. Faraday Soc.*, **27**, 51, 1931.

# MOLAR (MICELLAR) MASS, ELECTROVALENCY OF IONS AND OSMOTIC PRESSURE OF COLLOIDAL ELECTROLYTES.

By F. G. Donnan.

## 1. Introduction.

The general thermodynamic theory of membrane equilibria [1,2] indicates that under certain conditions measurements of osmotic pressure may yield fairly accurate estimates of the molar mass (or the mean

[1] F. G. Donnan and E. A. Guggenheim, *Z. physikal. Chem.* **162A.** 346, 1932.
[2] F. G. Donnan, *Z. physikal. Chem.*, **168A.** 369, 1934.

molar mass) of colloidal electrolytes. The object of this paper is to develop and summarise these simplifications of the general theory, and to show their application to a number of selected cases. For the sake of uniformity, it will be supposed always that water is the solvent. In the case of an ideal solution of any concentration the osmotic pressure $\pi$ is given by the equation $\pi = \dfrac{RT}{v_{H_2O}} \log \dfrac{1}{N_{H_2O}}$, where $v_{H_2O} = $ molar volume of water, $N_{H_2O} = $ mol fraction of water in the solution.[1] In the general case of a non-ideal solution, the foregoing equation becomes

$$\pi = \frac{gRT}{v_{H_2O}} \log \frac{1}{N_{H_2O}} \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \quad (1)$$

where $g$ is the osmotic coefficient of Bjerrum.[1] The considerations to follow will be mainly based on a simplified form of equation (1), applicable to sufficiently dilute solutions, combined with a simplified form of the general equation of ionic membrane equilibrium.

## 2. Monodisperse Singly Ionised Electrolyte.

Let us suppose that we have on one side of the semipermeable membrane pure water, on the other side an aqueous solution of the colloidal electrolyte ($G^{n+} + nCl^-$), where $G^{n+}$ denotes the non-permeating colloidal ion. We shall suppose that (a) the colloidal electrolyte consists solely of the ions $G^{n+}$ and $Cl^-$, (b) membrane hydrolysis is prevented or is negligible, (c) no change occurs in the state of aggregation of the colloidal cations. It need scarcely be remarked that the considerations to follow apply equally well, *mutatis mutandis*, to electrolytes of the types ($nNa^+ + G^{n-}$) or ($nH^+ + G^{n-}$), or to cases where the diffusible ions possess higher electrovalencies than one. For greater ease of printing, the colloidal cation $G^{n+}$ will be denoted by the symbol $G^+$ in the equations to follow. We have now

$$\pi v_{H_2O} = - gRT \log N_{H_2O} = - gRT \log (1 - N_{G^+} - N_{Cl^-}) \quad . \quad (2)$$

If the dilution is such that higher powers than the first of ($N_{G^+} + N_{Cl^-}$) may be neglected, equation (2) becomes

$$\pi v_{H_2O} = gRT(N_{G^+} + N_{Cl^-}). \qquad \cdot \qquad \cdot \qquad \cdot \quad (3)$$

Since $N_{Cl^-} = nN_{G^+}$, (3) becomes

$$\pi v_{H_2O} = gRT(n + 1)N_{G^+} = gRT(n + 1)N_{GCl_n}. \quad \cdot \qquad \cdot \quad (4)$$

In the case of sufficient dilution, we may now proceed as follows :

$$N_{G^+} = \frac{p_{G^+}}{p_{H_2O} + \Sigma p_i} = \frac{p_{G^+}/p_{H_2O}}{1 + \Sigma p_i/p_{H_2O}},$$

where the $p$'s denote mol numbers and $\Sigma p_i = p_{G^+} + p_{Cl^-}$. If we may neglect $\Sigma p_i/p_{H_2O}$ in comparison with unity, we obtain the further approximation $N_{G^+} = p_{G^+}/p_{H_2O}$, and therefore

$$N_{G^+}/v_{H_2O} = \frac{p_{G^+}}{p_{H_2O}v_{H_2O}} = m_{G^+},$$

where $m_{G^+}$ denotes the ratio of the number of mols of $G^+$ to the volume of free water in the solution. From (4) we have now

$$\pi = g(n + 1)RTm_{G^+} = g(n + 1)RTm_{GCl_n}. \qquad \cdot \qquad \cdot \quad (5)$$

Even if we know the value of $n$, (5) does not in general allow us to calculate the molar mass of $G^+$ from a measurement of $\pi$, since we do not know

the value of $g$, which may be considerably smaller than unity.* For example, the value of $g$ may be affected by the action of the coulomb field of the highly-charged $G^+$ ions on the $Cl^-$ ions, or by a variety of actions (*Hammarsten* effect). These difficulties might be surmounted if it were possible to make a sufficiently accurate series of measurements of $\pi$, enabling us to obtain a sufficiently accurate graphical extrapolation to the limit $m_{G^+} \to 0, g \to 1$. The theory of membrane equilibria, however, indicates a much more practical method of procedure.

## Correction for Hydration (Solvation).

In the foregoing considerations, $p_{H_2O}$ = number of mols of *free* water. If $p'_{H_2O}$ = total number of mols water, $p'_{H_2O} = p_{H_2O} + kp_{G^+}$, where $k$ = number of mols water bound per mol of $G^+$. Let $m'_{G^+}$ = molality of $G^+$ referred to *total* water ($m_{G^+}$ being the molality referred to free water), i.e.,

$$m'_{G^+} = \frac{p_{G^+}}{p'_{H_2O}v_{H_2O}}.$$

Then,

$$\frac{m_{G^+}}{m'_{G^+}} = \frac{p'_{H_2O}}{p_{H_2O}} = \frac{p_{H_2O} + kp_{G^+}}{p_{H_2O}} = 1 + k\frac{p_{G^+}}{p_{H_2O}} = 1 + km_{G^+}v_{H_2O} = 1 + hm_{G^+},$$

where $h = kv_{H_2O}$ = volume of water (reckoned as free water) bound per mol of $G^+$. We have now the two equations

$$\pi = g(n + 1)RTm_{G^+},$$
$$m'_{G^+} = \frac{m_{G^+}}{1 + hm_{G^+}}.$$

From the second equation $m_{G^+} = \dfrac{m'_{G^+}}{1 - hm'_{G^+}}$, and therefore

$$\pi = g(n + 1)RT\frac{m'_{G^+}}{1 - hm'_{G^+}}.$$

It is obvious from this equation that the hydration factor $h$ only affects higher powers of $m'_{G^+}$ than the first. If the dilution is such that these higher powers may be neglected in comparison with $m'_{G^+}$, then we may write

$$\pi = g(n + 1)RTm'_{G^+} = g(n + 1)RTm_{G^+}.$$

Such dilutions will, of course, be the more easily attained in practice the greater is the molar mass of $G^+$.

## Ionic Membrane Equilibrium.

Let us now suppose that $GCl_n$ in aqueous solution is separated from an aqueous solution of, say, NaCl by a membrane M permeable to all ions except $G^+$. The equilibrium state may be represented thus

$$\begin{array}{ccc|cc}
m'_{G^+} & G^+ & & & \\
m'_{Na^+} & Na^+ & & Na^+ & m''_{Na^+} \\
m'_{Cl^-} & Cl^- & & Cl^- & m''_{Cl^-} \\
(') & & M & ('') &
\end{array}$$

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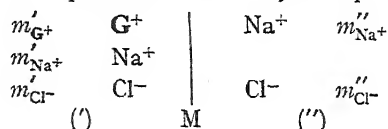
* If $G^+$ be an $n$-multiple aggregate of a simple univalent (monomeric) cation, then if $m$ denote molality *referred to* the *molar mass of this cation*, $m = nm_{G^+}$, and equation (5) becomes $\pi = g\dfrac{n + 1}{n}RTm$, which assumes the approximate form $\pi = gRTm$ if $n$ be sufficiently great compared with unity.

The single and double accents are used to distinguish quantities referring to the two solutions respectively. It is assumed that the NaCl is completely ionised, that no $Na^+$ is bound to $G^+$, and that binding of $H_2O$ to $Na^+$ may be neglected. If $P'$ and $P''$ denote the hydrostatic pressures at equilibrium, then with the previous assumptions as to dilution of $GCl_n$ it follows [2] that

$$\pi = P' - P'' = RT\{(n + 1)\, g'm'_{G^+} + 2g'm'_{Na^+} - 2g''m''_{Na^+}\}.$$

Let us now suppose that on either side of M the molality of NaCl is very much greater than that of $GCl_n$. Then at equilibrium $m'_{NaCl}$ will not differ much from $m''_{NaCl}$, and we may with sufficient approximation put $g' = g'' = \bar{g}$, where $\bar{g}$ may be taken as the mean value of $g$ for the two solutions of NaCl regarded as solutions of pure NaCl. It is clear that the molality of NaCl in relation to that of $G^+$ and its corresponding $Cl^-$ ions will require to be the greater, the greater is the value of $n$ (electrovalency of the colloidal ion $G^+$), in order that we may neglect the effect of $G^+$ and its equivalent $Cl^-$ ions on the ionic strength of solution ('). With this proviso we may now write

$$\pi = RT\bar{g}\,\{(n + 1)\, m'_{G^+} + 2m'_{Na^+} - 2m''_{Na^+}\} \quad . \quad . \quad (6)$$

Under these conditions we may consider the mean activity-coefficients of NaCl in the two solutions as sensibly equal, and write the equation of ionic membrane equilibrium in the form (approximate)

$$m'_{Na^+}\,(m'_{Na^+} + nm'_{G^+}) = (m''_{Na^+})^2, \text{ or}$$

$$\frac{(m'_{Na^+} - m''_{Na^+})\,(m'_{Na^+} + m''_{Na^+})}{m'_{Na^+}} = -\,nm'_{G^+} \quad . \quad . \quad (7)$$

From (6) and (7) we obtain

$$\pi = \bar{g}RT\left\{(n + 1)m'_{G^+} - \frac{2nm'_{G^+}}{1 + m''_{Na^+}/m'_{Na^+}}\right\} \quad . \quad . \text{ *(8)}$$

We may now, under the assumed conditions, write with sufficient approximation $m''_{Na^+}/m'_{Na^+} = 1$. In this case the negative "correction" term in the right-hand bracket reduces to $nm'_{G^+}$ (it does not vanish as is often stated), and we obtain the result

$$\pi = \bar{g}RTm'_{G^+} \qquad . \qquad . \qquad . \qquad . \qquad (9)$$

If we compare equations (5) and (9), two salient points will be noticed, namely

(1) The quantity $n$ has vanished from equation (9) (apparent non-ionisation of $GCl_n$).

(2) Instead of the unknown $g$ there appears in equation (9) a value $\bar{g}$ which we may regard as known.

It is thus possible by means of equation (9) to calculate from the corresponding (measured) value of $\pi$ a fairly accurate value for the molar mass of the colloidal ion $G^+$. In applying this procedure in practice, the question may arise as to the concentration of the simple electrolyte (NaCl in this case) which it is necessary to employ. Two methods may be used, according to convenience. Keeping the molality of $GCl_n$ constant, we may measure the equilibrium values of $\pi$ for a series of increasing molalities of NaCl, and employ the value of $\pi$ when it has fallen to a practically constant value. Or, keeping the value of the

* As pointed out by G. S. Hartley, this type of approximation is subject to a correction which, in effect, makes $\bar{g}$ equal to unity. The matter will be more fully discussed in a forthcoming paper.

NaCl molality constant, we may measure the equilibrium values of $\pi$ for a series of diminishing concentrations of $GCl_n$ and plot $\pi/c$ against $c$ (where $c =$ grms. $GCl_n$ per 100 grms. water). If we can extrapolate safely the value of $\pi/c$ to $c = 0$, then we may be sure that the excess of NaCl is sufficient. It must not be forgotten that, underlying the theory of the method is the assumption that $Na^+$ ions are not bound to $G^+$ and that $GCl_n$ remains always monodisperse, *i.e.*, that there occurs no aggregation of the colloidal ion $G^+$. We have also assumed that $GCl_n$ is completely ionised, *i.e.*, that no $Cl^-$ ions are bound to $G^+$. The case considered is, in fact, the *simplest* type of case where a fairly accurate determination of the molar mass of a colloidal ion from osmotic pressure measurements is possible. The principle of the method, namely, the employment of a " swamping " concentration of a simple electrolyte with freely diffusible ions, was first used by Sörensen[3] in his work on the osmotic pressures of protein solutions, whilst the theory (as applied to ideal very dilute solutions of ions) had been given some years previously.[4]

### 3. Monodisperse Multiply Ionised Electrolyte.

In this type of case, we shall not suppose, as in the former example, that the colloidal electrolyte yields in solution only two sorts of ions ; on the contrary, we shall suppose that the solution contains not only uncharged molecules (micelles), but also a large variety of ions of varying electric charge. Let us consider, for example, a colloidal acid whose molecule or micelle possesses a great number of $H^+$-ionisation points of varying ionising power, yielding a variety of micellar anions of different electrovalencies. Denoting the neutral or unionised molecule by $G_0$, and an anion by $G_i$, we have, with the same assumptions as in case (1),

$$\pi = gRT(m_{G_0} + \Sigma m_{G_i} + m_{H^+}).$$

Now, $m_{H^+} = \Sigma z_i m_{G_i}$, where $z_i =$ electrovalency (charge) of the anion $G_i$. Putting $m_{G_0} + \Sigma m_{G_i} = m_G$, the former expression for the osmotic pressure against pure water becomes

$$\pi = gRT(m_G + \Sigma z_i m_{G_i}) = gRT(m_G + m_{H^+}).$$

The presence of the term $\Sigma z_i m_{G_i}$, as well as that of the unknown osmotic coefficient $g$, renders it impossible in general to determine from this equation the micellar mass. If, however, we knew the value of $g$, an approximate knowledge of $m_{H^+}$ would enable us to determine an approximate value of $m_G$, and therefore an approximate value of the molar mass of $G_0$, since the molar masses of the various anions $G_i$ will not differ much from that of $G_0$.

Let us now consider the osmotic or membrane equilibrium where the aqueous solution of the colloidal acid is separated from an aqueous solution of pure HCl by a membrane M impermeable to $G_0$ and the anions $G_i$, as shown in the following diagram.

$$
\begin{array}{c|c}
G_0 & H^+ \\
H^+ & \\
\Sigma G_i & Cl^- \\
Cl^- & \\
(') \quad M & ('')
\end{array}
$$
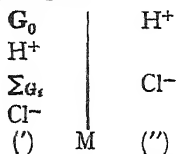
[3] S. P. L. Sörensen, *Compt. rend. trav. Lab. Carlsberg*, **12**, 1915-17 ; *Z. physiol. Chem.*, **106**. 43, 1919.
[4] F. G. Donnan, *Z. Elektrochem.*, **17**, 572, 1911.

On the side ($'$) we have the relation

$$m'_{H^+} = m'_{Cl^-} + \Sigma z_i m'_{G_i},$$

and therefore

$$m'_{G_0} + \Sigma m'_{G_i} + m'_{H^+} + m'_{Cl^-} = m'_G + \Sigma z_i m'_{G_i} + 2m'_{Cl^-}.$$

Assuming now that the molality of the HCl is greatly in excess of that of $G_0$ and the ions $G_i$, we may write the more general equation

$$\pi = RT\{g'm'_G + g'\Sigma z_i m'_{G_i} + 2g'm'_{Cl^-} - 2g''m''_{Cl^-}\}$$

in the approximate form

$$\pi = \bar{g}RT\{m'_G + \Sigma z_i m'_{G_i} + 2m'_{Cl^-} - 2m''_{Cl^-}\} \quad . \quad . \quad . \quad (10)$$

where $\bar{g}$ is the mean value of $g$ for the two solutions regarded as solutions of pure HCl. The approximate form of the equation of ionic membrane equilibrium is in this case

$$m_{Cl^-}(m'_{Cl^-} + \Sigma z_i m'_{G_i}) = (m''_{Cl^-})^2,$$

and this gives

$$2m'_{Cl^-} - 2m''_{Cl^-} = \frac{-2\Sigma z_i m'_{G_i}}{1 + m''_{Cl^-}/m'_{Cl^-}} \quad . \quad . \quad . \quad (11)$$

Combination of equations (10) and (11) gives

$$\pi = \bar{g}RT\left\{m'_G + \Sigma z_i m'_{G_i} - \frac{2\Sigma z_i m'_{G_i}}{1 + m''_{Cl^-}/m'_{Cl^-}}\right\}.$$

Putting now $m''_{Cl^-}/m'_{Cl^-} = 1$ approximately, we obtain finally,

$$\pi = \bar{g}RTm'_G \quad . \quad . \quad . \quad . \quad . \quad (12)$$

It is easy to see that from this equation we can, if the value of $\bar{g}$ be known, determine the molar mass of the colloidal acid $H_nG$. For let $w_0, w_1, w_2 \ldots$ be the masses per unit volume of water of $G_0$ and its various anions $G_i$, and let the corresponding molar masses be $M_0, M_1, M_2 \ldots$. Then

$$m'_G = m'_{G_0} + \Sigma m'_{G_i} = \frac{w_0}{M_0} + \frac{w_1}{M_1} + \frac{w_2}{M_2} + \ldots$$

Now, with good approximation, we may put $M_0 = M_1 = M_2 = \ldots$. Hence $m_G' = \dfrac{w_0 + w_1 + w_2 + \ldots}{M_0} = \dfrac{\text{mass concentration of } \textit{total } H_nG}{\text{molar mass of } H_nG}$

$= \dfrac{w}{M_0} =$ molar mass concentration of $\textit{total } H_nG$ (independent of ionisation), where $w =$ mass concentration of $\textit{total } H_nG$. Thus we get from equation (12) the equation

$$\pi = \bar{g}RT\frac{w}{M_0} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

from which $M_0$ can be calculated if we know $w$, $\pi$ and $\bar{g}$. If the colloidal acid were a weak acid, the relative excess of HCl might practically suppress its ionisation, so that in the case considered above $\Sigma m'_{G_i} = 0$ and therefore $m'_G = m'_{G_0}$, whence $\pi = \bar{g}RTm'_{G_0}$.

It will not be possible in general to make such an assumption, since a number of the $H^+$-ionisation points may be due to strongly acidic (e.g., sulphonic) groups. A few such groups in a large molecule (micelle) of unknown molar mass might give the impression of a relatively weak acid.

The employment of a relative excess of HCl may be deleterious in certain cases where the concentration of the acid may lead to a hydrolysis, e.g., breakage of glucosidic linkages in the case of certain complex gum acids. It is, however, not at all necessary to employ an acid. Any electrolyte with diffusible ions, which does not combine with, precipitate, or affect the aggregation of $G^+$, will do equally well. Consider, for example, the case of NaCl. The ionic membrane equilibrium will now be as shown in the annexed diagram,

$$
\begin{array}{c|c}
G_0 & H^+ \\
H^+ & \\
Na^+ & Na^+ \\
\Sigma G_i & Cl^- \\
Cl^- & \\
(') \quad M & ('')
\end{array}
$$
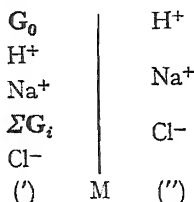
On the side (') we have

$$m'_{H^+} + m'_{Na^+} = m'_{Cl^-} + \Sigma z_i m'_{G_i} ,$$

and therefore

$$m'_{G_0} + \Sigma m'_{G_i} + m'_{H^+} + m'_{Na^+} + m'_{Cl^-} = m'_G + \Sigma z_i m'_{G_i} + 2m'_{Cl^-} \ldots \quad (14)$$

On the side ('') we have $m''_{H^+} + m''_{Na^+} = m''_{Cl^-}$, and therefore

$$m''_{H^+} + m''_{Na^+} + m''_{Cl^-} = 2m''_{Cl^-}. \ldots . \qquad . \qquad . \quad (15)$$

Equation (10) has therefore the same form as before.

For the ionic membrane equilibria of HCl and NaCl we have now the two respective equations

$$m'_{Cl^-}(m'_{Cl^-} + \Sigma z_i m'_{G_i} - m'_{Na^+}) = m''_{Cl^-}(m''_{Cl^-} - m''_{Na^+}),$$
$$m'_{Cl^-}(m'_{Cl^-} + \Sigma z_i m'_{G_i} - m'_{H^+}) = m''_{Cl^-}(m''_{Cl^-} - m''_{H^+}).$$

Addition of these two equations gives (using the relations (14) and (15))

$$m'_{Cl^-}(m'_{Cl^-} + \Sigma z_i m'_{G_i}) = (m''_{Cl^-})^2,$$

which is identical with equation (11). The rest of the reasoning is the same as before, so that we obtain again equation (12).

Let us now return to the equation for the osmotic pressure of the colloidal acid against pure water, i.e., the equation

$$\pi = gRT(m_G + \Sigma z_i m_{G_i}).$$

If we could make sufficiently accurate measurements of $\pi$ at constantly diminishing values of $m_G$, we might possibly be able to approach sufficiently near to the limit

$$g \to 1, \; m_{G_0} \to 0, \; \Sigma m_{G_i} = m_{G_i}, \; \Sigma z_i m_{G_i} = n m_{G_i},$$

where $m_{G_i}$ = molality of the *single* type of ion $G_i$ (i.e., the completely ionised micelle) and $n$ = number of $H^+$ ionisation points possessed by the neutral micelle. In the limit we have

$$\pi = RT(n + 1) \, m_{G_i},$$

Let $w_{G_i}$ = no. of grams $G_i$ per unit volume of water, $M$ = molar mass of $G_i$. Then the limiting equation becomes

$$\pi = RT \frac{n + 1}{M} \, w_{G_i}.$$

If we may very approximately identify the molar mass of $G_i$ with the molar mass of $G_0$ (the neutral unionised micelle), we may write

$$\pi = RT\frac{n+1}{M}w_{G_0}.$$

The object would be, by plotting $\pi/w_{G_0}$ against $w_{G_0}$, to be able to extrapolate graphically to $w_{G_0} \to 0$.* If successful, this would give the value of $\frac{n+1}{M}$. This expression contains, however, two unknowns, $n$ and $M$.

If we could titrate the acid with alkali to *complete* neutralisation, or analyse the neutral salt $Na_nG$, we could find the value of $n/M$, *i.e.*, the total number of ionisable H atoms per gram of dry acid. Call this value $a$. Then in the limit

$$\pi = RT\left(a + \frac{1}{M}\right)w_{G_0}, \quad \text{or} \quad M = \frac{1}{\mathrm{Lt}\,\dfrac{\pi}{RTw_{G_0}} - a}.$$

There might, however, be such a small difference between $\mathrm{Lt}\,\dfrac{\pi}{RTw_{G_0}}$ and $a$ that this method of determining $M$ would be impracticable. Suppose, for example, that $M = 10,000$, $n = 100$. Then

$$a = \frac{1}{100}, \; \frac{1}{M} = \frac{1}{10,000},$$

and therefore

$$\mathrm{Lt}\,\frac{\pi}{RTw_0} = a + \frac{1}{M} = \frac{1 \cdot 01}{100}.$$

In fact, we could write approximtely in the limit

$$\pi = RT\left(a + \frac{1}{M}\right)w_{G_0} = RTaw_{G_0},$$

so that within the practical limits of accuracy of the measurements the limiting value of $\pi/RTw_{G_0}$ would be given by the titration result $a$.

In this section we have considered the case of a multiply ionised colloidal acid and a series of equilibria $H_nG \rightleftharpoons xH^+ + (H_{n-x}G)^{x-}$ with $x = 1, 2 \ldots n$. We might equally well have considered the corresponding case of the multiply ionised alkali salt and the series of equilibria $Na_nG \rightleftharpoons xNa^+ + (Na_{n-x}G)^{x-}$. If the molar mass of $G$ be sufficiently large, there would still be a sufficiently good approximation in assuming a practically equal molar mass for the various types of micellar anions. In any case equation (12) will give a mean value. For

$$m'_G = m'_{G_0} + \Sigma m'_{G_i} = w/M,$$

where $w =$ mass concentration per unit volume of water of total salt, and $M =$ mean molar mass of $G_0$ and the various anions $G_i$.

Needless to say, the case of a multiply ionised colloidal salt of the type $GCl_n$ and the case of a multiply ionised colloidal base admit of exactly similar treatment.

## 4. Monodisperse Multiply Ionised Ampholyte.

Hitherto, we have assumed that the solution of the colloidal electrolyte contained either only colloidal cations or only colloidal anions. In

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* The higher the value of $n$, the more difficult it will be to extrapolate graphically to the limit from values of $w_{G_0}$ corresponding to practically measurable values of $\pi$.

the case of colloidal amphoteric electrolytes (colloidal ampholytes) there may be present in general both colloidal cations and colloidal anions, as well as simultaneously positively and negatively charged molecules (ions) with *net* zero charge (*zwitterionen*). The most familiar class of colloidal ampholytes is presented by the various proteins. In what follows, we shall denote a colloidal cation by the symbol $G_i^+$ and its molar concentration per unit volume of water by $m_{G_i}^+$. For a colloidal anion we shall write similarly $G_i^-$ and $m_{G_i}^-$. The unionised molecules and *zwitterions* will be denoted indifferently by the symbol $G_0$, and the *sum* of the molar concentrations (per unit volume of water) of the unionised molecules plus the *zwitterions* by the symbol $m_{G_0}$.

We shall now consider the case of membrane equilibrium where the colloidal ampholyte is separated by a membrane M from a solution of HCl, as shown in the annexed diagram.

$$
\begin{array}{c|c}
\begin{array}{l}
G_0 \\
H^+ \\
\Sigma G_i^+ \\
\Sigma G_i^- \\
Cl^-
\end{array}
&
\begin{array}{l}
H^+ \\
\ \\
Cl^- \\
\ 
\end{array}
\\
(') \quad M \quad ('')
\end{array}
$$
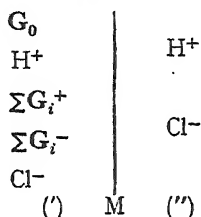
We shall suppose that the concentration of $H^+$ is such that we may neglect that of $OH^-$, but we shall not suppose in general that $\Sigma(m_{G_i}^-)'$ is negligible in comparison with $\Sigma(m_{G_i}^+)'$.

On the side (') we have $m'_{H^+} + \Sigma(z_i m_{G_i}^+)' = m'_{Cl^-} + \Sigma(z_i m_{G_i}^-)'$, and therefore

$$m'_{G_0} + \Sigma(m_{G_i}^+)' + \Sigma(m_{G_i}^-)' + m'_{H^+} + m'_{Cl^-}$$
$$= m'_G + \Sigma(z_i m_{G_i}^-)' - \Sigma(z_i m_{G_i}^+)' + 2m'_{Cl^-},$$

where $\qquad m'_G = m'_{G_0} + \Sigma(m_{G_i}^+)' + \Sigma(m_{G_i}^-)'$.

Equation (10) has now the form (assuming relative molar excess of HCl),

$$\pi = \bar{g}RT\{m'_G + \Sigma(z_i m_{G_i}^-)' - \Sigma(z_i m_{G_i}^+)' + 2m'_{Cl^-} - 2m''_{Cl^-}\} \quad . \ (16)$$

Similarly, the equation of ionic membrane equilibrium for HCl is now

$$m'_{Cl^-}\{m'_{Cl^-} + \Sigma(z_i m_{G_i}^-)' - \Sigma(z_i m_{G_i}^+)'\} = (m''_{Cl^-})^2 \quad . \qquad . \ (17)$$

and this gives

$$2m'_{Cl^-} - 2m''_{Cl^-} = \frac{-2\{\Sigma(z_i m_{G_i}^-)' - \Sigma(z_i m_{G_i}^+)'\}}{1 + m''_{Cl^-}/m'_{Cl^-}}. \ldots \qquad . \ (18)$$

Combining equations (16) and (18), we obtain

$$\pi = \bar{g}RT\left[ m'_G + \Sigma(z_i m_{G_i}^-)' - \Sigma(z_i m_{G_i}^+)' - \frac{2\{\Sigma(z_i m_{G_i}^-)' - \Sigma(z_i m_{G_i}^+)'\}}{1 + m''_{Cl^-}/m'_{Cl^-}} \right]$$

which, with the relation $m''_{Cl^-}/m'_{Cl^-} \sim$, gives finally

$$\pi = \bar{g}RTm'_G,$$

or

$$\pi = \bar{g}RT\{m'_{G_0} + \Sigma(m_{G_i}^+)' + \Sigma(m_{G_i}^-)'\}. \qquad . \qquad . \ (19)$$

Let $M$ be the molar mass (taken as practically the same) for $\mathbf{G_0}$ and any $\mathbf{G}_s^+$ or $\mathbf{G}_s^-$, and let $w =$ mass of dry ampholyte per unit volume of water. Then, equation (19) becomes simply $\pi = \bar{g}RT\dfrac{w}{M}$.

From this equation the value of $M$ can be calculated, assuming $\pi$ and $\bar{g}$ as known. As in previously discussed instances, we assume that $\bar{g}$ is the mean value of $g$ for the two solutions (') and (''), regarded as pure solutions of HCl.

From this discussion it will be obvious that the apparently very complicated case of a multiply ionised monodisperse ampholyte offers no special difficulties.

Let us suppose now that the $H^+$ concentration in (') is such that the condition $\sum(z_i m_{G_i}^+)' = \sum(z_i m_{G_i}^-)'$ is satisfied, i.e. that the total positive charge carried by the colloidal cations is equal to the total negative charge carried by the colloidal anions. This gives $m'_{H^+} = m'_{Cl^-}$. If we do not assume that the corresponding molality of HCl in (') is largely in excess of $m'_G$, we obtain instead of equations (16) and (17) the more general equations

$$\pi = RT\{g'm'_G + 2g'm'_{Cl^-} - 2g''m''_{Cl^-}\} \qquad . \qquad . \quad (20)$$

and

$$f'_{HCl}(m'_{Cl^-})^2 = f''_{HCl}(m''_{Cl^-})^2 \qquad . \qquad . \qquad . \quad (21)$$

where $f_{HCl}$ denotes the mean activity-coefficient of the ions of HCl. If we now introduce the approximation

$$\frac{m'_{Cl^-}}{m''_{Cl^-}} = \sqrt{\frac{f''_{HCl}}{f'_{HCl}}} = 1$$

equation (20) may be written in the approximate form

$$\pi = RT\{g'm'_G + 2m'_{Cl^-}(g' - g'')\} \qquad . \qquad . \qquad . \quad (22)$$

Equation (22) reduces to the form

$$\pi = g'RTm'_G \qquad . \qquad . \qquad . \qquad . \quad (23)$$

only if we may neglect the term $2m'_{Cl^-}(g' - g'')$ in comparison with $g'm'_G$. Even then the equation (23) contains an unknown osmotic coefficient $g'$. It will be obvious that the foregoing series of assumptions (approximations) are in general unsatisfactory. If, however, the molality of HCl in (') required to determine the iso-electric condition

$$\sum(z_i m_{G_i}^+)' = \sum(z_i m_{G_i}^-)'$$

were such that it is largely in excess of $m'_G$, then we have instead of equations (20) and (21) the equations

$$\pi = \bar{g}RT\{m'_G + 2m'_{Cl^-} - 2m''_{Cl^-}\} \qquad . \qquad . \qquad . \quad (24)$$

and

$$(m'_{Cl^-})^2 = (m''_{Cl^-})^2 \qquad . \qquad . \qquad . \qquad . \quad (25)$$

whence

$$\pi = \bar{g}RTm'_G . \qquad . \qquad . \qquad . \qquad . \quad (26)$$

where $\bar{g}$ denotes the mean value of $g$ for the two solutions regarded as solutions of pure HCl.

The safest method, however, is to have in (') a concentration of HCl sufficient to determine (or nearly determine) the iso-electric condition, and also a " swamping " concentration of a simple neutral electrolyte with diffusible ions, such as NaCl. Equations (24) and (25) become then

good approximations, and lead to equation (26), but in this case $\bar{g}$ must be regarded as the mean value of $\bar{g}$ for the two solutions regarded mainly as pure solutions of NaCl (or, more strictly, NaCl + HCl).    If in this case we make the approximation $\bar{g} = 1$, justified perhaps by the fact that, owing to the high molar mass of the ampholyte and its *zwitterions* and ions, the absolute concentrations of HCl and NaCl in (') and ('') may be small, we arrive at the result

$$\pi = RTm'_G = RT\{m'_{G_0} + \Sigma(m^+_{G_i})' + \Sigma(m^-_{G_i})'\},$$

from which the molar mass can be calculated, as explained previously. These remarks will suffice to explain the theory of the method, first employed by Sörensen,[5] for determining the molar mass of protein ampholytes from measurements of osmotic pressure.   It is fortunate, as shown more especially in recent years by the excellent work of Svedberg,[6] Pauli,[7] and Adair,[8] that the pure natural protein ampholytes remain monodisperse within definite ranges of $p_H$ and in the presence of sufficient concentrations of simple electrolytes with diffusible ions.   This fact has greatly simplified the study of solutions of the pure natural proteins, since variable dispersity introduces a complicating factor into the equations.   An example of this will be discussed in the next section.

### 5. Polydisperse Multiply Ionised Electrolyte.

As an example of this type of case, we shall consider solutions of the sodium salt of a multivalent anion of variable dispersity.  We may represent this as a series of equilibria of the type

$$p\mathrm{Na}_n\mathrm{G} \rightleftharpoons xp\mathrm{Na}^+ + (\mathrm{Na}_{(n-x)p}\mathrm{G}_p)^{xp-},$$
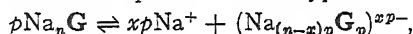
with $xp = 1, 2, 3 \ldots np, p = 1, 2, 3 \ldots p$.  If we put $xp = y, np = m,$ we may write this series also

$$\mathrm{Na}_m\mathrm{G}_p \rightleftharpoons y\mathrm{Na}^+ + (\mathrm{Na}_{m-y}\mathrm{G}_p)^{y-},$$
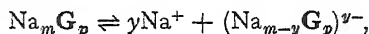
with $y = 1, 2, 3 \ldots m, p = 1, 2, 3 \ldots p$.

For any degree of " aggregation " determined by the value of $p$, $y$ indicates a particular stage of ionisation.

We shall denote the neutral molecule or micelle $\mathrm{Na}_m\mathrm{G}_p$ by the symbol $\mathrm{G}_{0p}$, and its molar concentration per unit volume of water by the symbol $m_{\mathrm{G}_{0p}}$.   Similarly, the anion $\mathrm{Na}_{m-y}\mathrm{G}_p$ will be denoted by $\mathrm{G}_{py}$, and its molar concentration by $m_{\mathrm{G}_{py}}$.   Then, with the same assumptions as to dilution as in previous cases, the value of $\pi$, the osmotic pressure against pure water, will be given by the equation

$$\pi = gRT(\sum_p m_{\mathrm{G}_{0p}} + \sum_p \sum_y m_{\mathrm{G}_{py}} + \sum_p \sum_y z_{py} m_{\mathrm{G}_{py}}),$$

where $z_{py}$ = electric charge (electrovalency) of the anion $\mathrm{Na}_{m-y}\mathrm{G}_p$, since $m_{\mathrm{Na}^+} = \sum_p \sum_y z_{py} m_{\mathrm{G}_{py}}.$

Now consider the case where we have the colloidal electrolyte on side (') and NaCl present on both sides with a molality in each case very much

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[5] Compare, for example, the summary of his work given by Sörensen in his book, *Proteins : Lectures given in the United States in* 1924 (the Fleischmann Laboratories, 1925).

[6] For a recent brief summary of this work, see *Chemical Reviews*, **14**, 1, 1934
[7] Summarised in *Kolloidchemie der Eiweisskörper* by Wo. Pauli and E. Valkó (Steinkopff, Dresden, 1933).

[8] *Proc. Roy. Soc.*, **109A**, 292, 1925 ; *ibid.*, **108A**, 627, 1925 ; *ibid.*, **120A**, 573, 1928 ; *Biochemical J.*, **24**, 1864, 1930 ; *ibid.*, **26**, 1811, 1932.

greater than that of the colloidal electrolyte. Then, with the previous notation we get

$$\pi = \bar{g}RT(\sum_p m'_{G_{0p}} + \sum_p \sum_y m'_{G_{py}} + \sum_p \sum_y z_{py}m'_{G_{py}} + 2m'_{Cl^-} - 2m''_{Cl^-}).$$

As before, we write

$$m'_{Na^+} \cdot m'_{Cl^-} = m''_{Na^+} \cdot m''_{Cl^-} = (m''_{Cl^-})^2,$$

or

$$m'_{Cl^-}(m'_{Cl^-} + \sum_p \sum_y z_{py}m'_{G_{py}}) = (m''_{Cl^-})^2,$$

since

$$m'_{Na^+} = m'_{Cl^-} + \sum_p \sum_y z_{py}m'_{G_{py}}.$$

This gives

$$2(m'_{Cl^-} - m''_{Cl^-}) = \dfrac{-2\sum_p \sum_y z_{py}m'_{G_{py}}}{1 + m''_{Cl^-}/m'_{Cl^-}},$$

and therefore

$$\pi = \bar{g}RT\left(\sum_p m'_{G_{0p}} + \sum_p \sum_y m'_{G_{py}} + \sum_p \sum_y z_{py}m'_{G_{py}} - \dfrac{2\sum_p \sum_y z_{py}m'_{G_{py}}}{1 + m''_{Cl^-}/m_{Cl^-}}\right)$$

Putting approximately $m''_{Cl^-}/m'_{Cl^-} = 1$, we obtain

$$\pi = \bar{g}RT(\sum_p m'_{G_{0p}} + \sum_p \sum_y m'_{G_{py}})$$
$$= \bar{g}RT\{\sum_p (m'_{G_{0p}} + \sum_y m'_{G_{py}})\}.$$

Now, $m'_{G_{0p}} + \sum_y m'_{G_{py}} =$ the sum of the molalities of a particular undissociated micelle $Na_m G_p$, and its micellar anions (corresponding to a particular value of $p$). Call this $m'_{G_p}$. Then we may write $\pi = \bar{g}RT\sum_p m'_{G_p}$. Both $m'_{G_p}$ and $p$ will vary with concentration and $p$ will vary in general with the concentration of NaCl.

Now $m'_{G_p} = \dfrac{w_0}{M_0} + \dfrac{w_1}{M_1} + \dfrac{w_2}{M_2} + \ldots$, where $w_0, w_1, w_2 \ldots$ are the masses per unit volume of water of a particular undissociated $Na_m G_p$ and its various micellar anions, and $M_0, M_1, M_2 \ldots$ are the corresponding molar masses. If $m$Na is sufficiently small in comparison with $p$G we may put approximately $M_0 = M_1 = M_2 \ldots$, and therefore $m'_{G_p} = \dfrac{\text{mass concentration of a } total \text{ particular } Na_m G_p}{\text{molar mass of this } Na_m G_p} = $ molar concentration of this total $Na_m G_p$, i.e., independent of the ionisation of the $Na_m G_p$. Hence $\sum_p m'_{G_p} =$ molar concentration of all the total $Na_m G_p$ varieties present (corresponding to the values of $p$) and independent of their various ionisations. Let $m'_G =$ molar concentration of total $Na_m G$, i.e., of the simplest molecule, which we shall suppose corresponds to $p = 1$. Then $\sum_p m'_{G_p} = m'_G \sum_p$, and we have

$$\pi = \bar{g}RTm'_G \sum_p. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (27)\ *$$

From equation (27) we see that in this case $\pi$ depends on the aggregation coefficient $\sum_p$ as well as on the osmotic coefficient $\bar{g}$. If the

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*It is, of course, assumed in equation (27) that none of the anions except Cl⁻ can pass through the membrane. In certain cases this condition may not be satisfied (e.g., the alkali salts of the higher aliphatic acids).

former varies with the concentration of NaCl, then clearly the molar or micellar mass calculated from equation (27) will depend on the concentration of NaCl employed in the experiment.[9] On the other hand, given the molar mass of $Na_mG$ (*i.e.*, $Na_nG$) as known, we may employ equation (27) for the purpose of determining how $\Sigma_p$ varies with the concentration of NaCl, always assuming, of course, that the molarity of NaCl is sufficiently high to justify the approximation $m''_{Cl^-}/m'_{Cl^-} \sim 1$. If the colloidal electrolyte is not sufficiently lyophile (hydrophile in this case), the success of this method may be endangered by precipitation of the colloidal electrolyte before sufficiently high molalities of NaCl (or other simple electrolyte with diffusible ions) can be attained. It will work best when the colloidal electrolyte possesses a sufficient number of strongly hydrophile groups to prevent too great sensitivity (aggregation tendency) in the presence of other electrolytes.

It will not be necessary to devote a separate section to the case of a polydisperse multiply ionised ampholyte, since this type is easily dealt with by a combination of the procedure given in the present section with that given in section 4. The required formulation may be left to the reader.

### 6. Calculation of the Ion-Difference Term from Membrane Potentials.

Let us take, as an example, the case discussed in Section 2 and the equation there obtained for $\pi$, *i.e.*,

$$\pi = RT\bar{g}\{(n+1)m'_{G^+} + 2m'_{Na^+} - 2m''_{Na^+}\}$$

The ion-difference term $RT\bar{g}(2m'_{Na^+} - 2m''_{Na^+})$, which may be called the " ion-difference pressure," represents the " correction term " for the unequal distribution of the diffusible ions $Na^+$ and $Cl^-$. If we denote by $\psi'$ and $\psi''$ the (positive) electrical potentials of solutions (') and (") respectively at equilibrium, and write $\psi = \psi' - \psi''$, where $\psi$ is commonly called the " membrane potential," then for sufficiently dilute solutions we have [2]

$$- \psi = \frac{RT}{F} \log \frac{f'_{Na^+} \cdot m'_{Na^+}}{f''_{Na^+} \cdot m''_{Na^+}}.$$

In this case, since the two solutions differ only slightly in concentration of NaCl and the molality of the colloidal electrolyte is relatively small, we may put approximately $f'_{Na^+} = f''_{Na^+}$. Hence

$$- \frac{F\psi}{RT} = \log \frac{m'_{Na^+}}{m''_{Na^+}} = \log \left( 1 + \frac{m'_{Na^+} - m''_{Na^+}}{m''_{Na^+}} \right)$$

or $\qquad m'_{Na^+} - m''_{Na^+} = m''_{Na^+}(e^{-F\psi/RT} - 1).$

Since $F\psi/RT$ is small in this case, we may write

$$m'_{Na^+} - m''_{Na^+} = - m''_{Na^+}\frac{F\psi}{RT}$$

and therefore

$$\pi = RT\bar{g}\left\{(n+1)m'_G - 2m''_{Na^+}\frac{F\psi}{RT}\right\}.$$

[9] In this connection, reference may be made to the important work of Conmar Robinson and his collaborators, summarised in the paper " The Nature of the Aqueous Solutions of Dyestuffs " (this volume, No. 23).

If we measure $m''_{\mathrm{Na+}}$ and $\psi$, we may use this equation to calculate, from a measurement of $\pi$, the part of the osmotic pressure due to the ions of the colloidal electrolyte, *i.e.*, the part $RT\bar{g}(n + \mathrm{I})m'_{\mathrm{G}}$. We cannot, however, calculate $m'_{\mathrm{G}}$ in this way unless we know also the value of $n$, *i.e.*, the electrovalency of the colloidal cation $\mathbf{G^+}$.

Let us now apply the foregoing reasoning to the case discussed in Section 3. Here we have the corresponding equation

$$\pi = \bar{g}RT\{m'_{\mathrm{G}} + \textstyle\sum z_i m'_{\mathrm{G}i} + 2m'_{\mathrm{Cl-}} - 2m''_{\mathrm{Cl-}}\}.$$

Treated in the same way, this gives

$$\pi = \bar{g}RT\left\{m'_{\mathrm{G}} + \textstyle\sum z_i m'_{\mathrm{G}i} + 2m''_{\mathrm{Cl-}}\frac{F\psi}{RT}\right\}$$

A sufficiently accurate knowledge of $\pi$, $\psi$, $\bar{g}$, and $m''_{\mathrm{Cl-}}$ would give the value of $m'_{\mathrm{G}} + \sum z_i m'_{\mathrm{G}i}$, *i.e.*, of $m'_{\mathrm{G}_o} + \sum m'_{\mathrm{G}i} + \sum z_i m_{\mathrm{G}i}$, but we cannot in general determine in this way the value of $m'_{\mathrm{G}_o} + \sum m'_{\mathrm{G}i}$, since we do not know the value of the term $\sum z_i m'_{\mathrm{G}i}$. Just as in the previous case, however, the value of $m'_{\mathrm{G}} + \sum z_i m'_{\mathrm{G}i}$ will give us that part of the osmotic pressure which is due to the colloidal electrolyte and its ions.

An interesting possibility arises when we apply this procedure to the case of an ampholyte discussed in Section 4.

The corresponding equation

$$\pi = \bar{g}RT\{m'_{\mathrm{G}} + \textstyle\sum(z_i m_{\mathrm{G}i}-)' - \sum(z_i m_{\mathrm{G}i}+)' + 2m'_{\mathrm{Cl-}} - 2m''_{\mathrm{Cl-}}\},$$

becomes now

$$\pi = \bar{g}RT\left\{m'_{\mathrm{G}} + \textstyle\sum(z_i m_{\mathrm{G}i}-)' - \sum(z_i m_{\mathrm{G}i}+)' + 2m''_{\mathrm{Cl-}}\frac{F\psi}{RT}\right\}.$$

If the ampholyte is near the iso-electric point, the quantity

$$\textstyle\sum(z_i m_{\mathrm{G}i}-)' - \sum(z_i m_{\mathrm{G}i}+)'$$

will be small, so that we may write approximately

$$\pi = \bar{g}RT\left\{m'_{\mathrm{G}} + 2m''_{\mathrm{Cl-}} \cdot \frac{F\psi}{RT}\right\}.$$

In this case, sufficiently accurate determinations of $\pi$, $m''_{\mathrm{Cl-}}$ and $\psi$ may give a value for $m'_{\mathrm{G}}$ or $m'_{\mathrm{G}_o} + \sum(m_{\mathrm{G}i}+)' + \sum(m_{\mathrm{G}i}-)'$, and hence for the molar mass (or mean molar mass) of the ampholyte, though, of course, the value of $\psi$ will be very small.

### 7. Electrovalency of Colloid Ions.

In the case considered in Section 2, we have seen from the discussion in Section 6 that we may write

$$m'_{\mathrm{Na+}} - m''_{\mathrm{Na+}} = -\frac{F\psi}{RT}m''_{\mathrm{Na+}}.$$

Also (see Section 2), we may write

$$m'_{\mathrm{Na+}} - m''_{\mathrm{Na+}} = \frac{-nm'_{\mathrm{G+}}}{\mathrm{I} + m''_{\mathrm{Na+}}/m'_{\mathrm{Na+}}} = -\frac{nm'_{\mathrm{G+}}}{2}.$$

Combining the last two equations with the equation $\pi = \bar{g}RTm'_{\mathrm{G+}}$, we obtain

$$n = \frac{2\bar{g}F\psi}{\pi}m''_{\mathrm{Na+}}.$$

This equation gives the value of $n$, provided we possess sufficiently accurate measurements of $\pi$, $\psi$ and $m''_{Na^+}$.

We will now apply the same method of reasoning to the case considered in Section 3. We have now

$$m'_{Cl^-} - m''_{Cl^-} = \frac{-\sum z_i m'_{G_i}}{2}.$$

If $\psi$ denote *negative* potential, then

$$\psi' - \psi'' = \psi = \frac{RT}{F} \log \frac{m''_{Cl^-}}{m'_{Cl^-}},$$

and hence

$$-\psi = \frac{RT}{F} \log \frac{m'_{Cl^-}}{m''_{Cl^-}} = \frac{RT}{F} \frac{m'_{Cl^-} - m''_{Cl^-}}{m''_{Cl^-}},$$

or

$$m'_{Cl^-} - m''_{Cl^-} = -\frac{F\psi}{RT} m''_{Cl^-}.$$

Combining these equations, we obtain

$$\sum z_i m'_{G_i} = \frac{2F\psi}{RT} m''_{Cl^-}.$$

Denoting by $Z_i$, the *mean* electrovalency of the $G_i$ anions under the given conditions, we have

$$\frac{\sum z_i m'_{G_i}}{\sum m'_{G_i}} = Z_i.$$

Since in this case $\pi = \bar{g}RT(m'_{G_0} + \sum m'_{G_i})$, it follows that

$$\frac{\pi}{\bar{g}RT} = m'_{G_0} + \sum m'_{G_i} = m'_{G_0} + \frac{\sum z_i m'_{G_i}}{Z_i} = m'_{G_0} + \frac{2F\psi}{RTZ_i} m''_{Cl^-},$$

or

$$\pi = \bar{g}\left(RT m'_{G_0} + \frac{2F\psi}{Z_i} m''_{Cl^-}\right).$$

Only in the case that $m'_{G_0}$ is zero or very small may we write

$$\frac{\pi}{\bar{g}} = \frac{2F\psi}{Z_i} m''_{Cl^-}$$

or

$$Z_i = \frac{2F\psi\bar{g}}{\pi} m''_{Cl^-},$$

an equation from which $Z_i$ can be calculated if we possess sufficiently accurate data for $\psi$, $\pi$, and $m''_{Cl^-}$.

Let us now apply this procedure to the case of the ampholyte considered in Section 4. We have now

$$m'_{Cl^-} - m''_{Cl^-} = \frac{-\{\sum(z_i m^-_{G_i})' - \sum(z_i m^+_{G_i})'\}}{1 + m''_{Cl^-}/m'_{Cl^-}}$$

$$= -\tfrac{1}{2}\{\sum(z_i m^-_{G_i})' - \sum(z_i m^+_{G_i})'\},$$

and also

$$m'_{Cl^-} - m''_{Cl^-} = -\frac{F\psi}{RT} m''_{Cl^-}.$$

Hence

$$\sum(z_i m^-_{G_i})' - \sum(z_i m^+_{G_i})' = \frac{2F\psi}{RT} m''_{Cl^-}.$$

If we define a quantity $Z_i$, which we may term the *mean positive ion-electrovalency*, by means of the equation

$$\frac{\Sigma(z_i m_{G_i}^+)' - \Sigma(z_i m_{G_i}^-)'}{\Sigma(m_{G_i}^+)' + \Sigma(m_{G_i}^-)'} = Z_i,$$

then it follows that

$$\Sigma(m_{G_i}^+)' + \Sigma(m_{G_i}^-)' = -\frac{2F\psi}{RTZ_i} \cdot m_{Cl^-}''$$

From the equation $\pi = \bar{g}RT\{m_{G_o}' + \Sigma(m_{G_i}^+)' + \Sigma(m_{G_i}^{-\prime})\}$

and the foregoing equation we obtain the result:

$$\pi = \bar{g}\left(RTm_{G_o}' - \frac{2F\psi}{Z_i} \cdot m_{Cl^-}''\right).$$

Only in the case that $m_{G_o}'$ is negligibly small may we write

$$Z_i = -\bar{g} \cdot \frac{2F\psi}{\pi} \cdot m_{Cl^-}'',$$

an equation from which $Z_i$ can be calculated if we possess sufficiently accurate values of $\psi$, $\pi$, and $m_{Cl^-}''$. Concerning the experimental methods of determining membrane potentials reference may be made to the earlier work of Loeb [10] and the later work of Adair.[11]

In connection with the equations contained in this section and in Section 6 it may be remarked that the values of $\psi$ will be small and difficult to determine accurately. The objection might be urged that it would be easier and more accurate to calculate the values of $\psi$ from analytical determinations of the concentrations of the diffusible ions (Cl⁻ or Na⁺ in the cases discussed), since the activity-coefficients of these ions have been assumed to be equal on both sides of the membrane. Owing to adsorptions or other types of binding, the analytical results may not, however, give correct concentrations of the free ions.

## 8. Remarks on some Approximations made in Section (1).

In deducing equations (3) and (4) it was assumed that higher powers of $(N_{G^+} + N_{Cl^-})$ than the first could be neglected. Let us now suppose that this approximation will suffice for $N_{G^+}$ owing to the high molar mass of $G^+$, but perhaps not for $N_{Cl^-}$ owing to a possibly high value of $n$ (case of a very highly charged colloidal cation). Then from (2) we get (retaining the second power in the expansion)

$$\pi v_{H_2O} = gRT\{(N_{G^+} + N_{Cl^-}) + \tfrac{1}{2}(N_{G^+} + N_{Cl^-})^2\}.$$

Putting $\quad (N_{G^+} + N_{Cl^-})^2 = N_{G^+}^2 + 2N_{G^+}N_{Cl^-} + N_{Cl^-}^2$

$$= N_{Cl^-}(2N_{G^+} + N_{Cl^-}), \quad \text{and} \quad N_{Cl^-} = nN_{G^+},$$

we have $\qquad\qquad (N_{G^+} + N_{Cl^-})^2 = n(n+2)N_{G^+}^2.$

[10] *Proteins and the Theory of Colloidal Behaviour*, by Jacques Loeb (New York. 1924).
[11] Concerning the determination of the membrane potentials of protein solutions and the valency of protein ions, see G. S. Adair and M. E. Adair, *Biochemical J.*, **28**, 199, 1934.

Equation (4) now becomes $\pi v_{H_2O} = gRTN_{G^+}\{n + 1 + \tfrac{1}{2}n(n + 2)N_{G^+}\}$.

Now $N_{G^+} = \dfrac{p_{G^+}}{p_{H_2O} + \Sigma p_i}$, where in this case $\Sigma p_i = p_{G^+} + p_{Cl^-} = (n + 1)p_{G^+}$.

Hence $N_{G^+} = \dfrac{p_{G^+}/p_{H_2O}}{1 + (n + 1)p_{G^+}/p_{H_2O}}$, and therefore $\dfrac{N_{G^+}}{v_{H_2O}} = \dfrac{m_{G^+}}{1 + (n + 1)r}$,

where $r = p_{G^+}/p_{H_2O}$. If we may write with sufficient approximation $N_{G^+}/v_{H_2O} = m_{G^+}$, we obtain

$$\pi = gRTm_{G^+}\{n + 1 + \tfrac{1}{2}n(n + 2)N_{G^+}\}.$$

If $n$ be much greater than 2 (say $n \geqq 100$), we may write approximately $\pi = gRTnm_{G^+}(1 + \tfrac{1}{2}nN_{G^+})$, or $\pi/m_{G^+} = gRTn(1 + \tfrac{1}{2}nN_{G^+})$. The greater the value of $n$ for a given molar mass of $G^+$, the smaller must be the value of $m_{G^+}$ in order that we may write with sufficiently high approximation $\pi/m_{G^+} = gRTn$. To take a perhaps possible example, let us suppose the molar mass of $G^+$ to be 10,000, and the value of $n$ to be 100. For a 10 per cent. solution of $G^+$, made up from 100 grams plus 1000 c.c. water, we have present

$$\text{mols } G^+ = 1/100$$
$$\text{mols } Cl^- = 1$$
$$\text{mols } H_2O = 56,$$

and hence                 $N_{G^+} = 1/5700 = 1/6000$, say.

Then $nN_{G^+} = 1/60$, $\tfrac{1}{2}nN_{G^+} = 1/120$, and $\pi/m_{G^+} = 100gRT$ (1·0083). The neglect of the term $\tfrac{1}{2}nN_{G^+}$ will therefore cause an error of approximately 1 per cent. in the 10 per cent. solution. At very low values of $m_{G^+}$, which will require to be the lower the greater the value of $n$ owing to the electrical forces between $G^+$ and the $Cl^-$ ions, we must eventually *approach* the limit $g \to 1$ and $\pi/m_{G^+} = RT(n + 1)$. As the concentration rises, $g$ will decrease but the term $\tfrac{1}{2}n(n + 2)N_{G^+}$ will increase. A graphical plot of $\pi/m_{G^+}$ against $m_{G^+}$, if it were possible down to low enough values of $m_{G^+}$, would show a curve tending to become horizontal at low values of $m_{G^+}$, but with increasing values of $m_{G^+}$ *possibly* exhibiting first a minimum and then a gradual rise. Nothing very definite, however, can be stated unless we know in any particular case the form of the function $g = \phi(m_{G^+})$, a knowledge of which can only be obtained from an extension of the theories of Debye, Hückel, and Onsager to highly charged multivalent colloidal ions.[12]

## 9. Conclusion.

It will have been observed that in the equations given in this paper, no assumptions have been made concerning the functional forms of any ionisation or adsorption equilibria. Although the equations have been put, in general, in the form of multiple ionisations of more or less well-defined molecular or " micellar " species, allowance has been made for variable aggregation, and correction terms can easily be introduced for any adsorptions or other linkages of diffusible ions which have been neglected. The main conclusions to be derived from the method pursued are, however, really independent of any specially " chemical " formulation of colloidal electrolytes, and are not essentially affected by the consideration, or want of consideration, of molecular or ionic adsorptions.

[12] See, for example, P. van Rysselberghe, *J. Physical Chem.*, **38**, 645, 1934. Also a paper (this volume, No. 6) by G. S. Hartley on the Debye-Hückel theory and colloidal electrolytes.

This can be shown very simply in the following way. In the annexed membrane equilibrium diagram

$$
\begin{array}{c|c}
(\Sigma G)' & \\
 & (\Sigma i)'' \\
(\Sigma i)' & \\
\multicolumn{2}{c}{M} \\
(') & ('')
\end{array}
$$
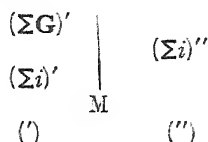
the symbol $\Sigma G$ denotes the sum of the colloidal (non-diffusible) particles, whether electrically neutral, positively charged, or negatively charged, whilst the symbol $\Sigma i$ denotes the sum of the positive and negative diffusible ions. With the same assumptions as to dilution (discussed in Section 1), we have in general

$$\pi = RT(g'\Sigma m'_G + g'\Sigma m'_i - g''\Sigma m''_i).$$

We suppose now that $\Sigma m'_i$ and $\Sigma m''_i$ are relatively much greater than $\Sigma m'_G$, so that we may write with sufficient approximation $g' = g''$. The previous equation becomes then

$$\pi = \bar{g}RT(\Sigma m'_G + \Sigma m'_i - \Sigma m''_i).$$

Now, for any ionic species $i$ in sufficiently dilute solution, we have in general,[2]

$$\frac{f'_i m'_i}{f''_i m''_i} = e^{\frac{z_i F \psi}{RT}}$$

where $z_i$ denotes its electrovalency (now taken positive for positive ions, and negative for negative ions), and $\psi =$ positive potential of solution $('')$ minus positive potential of solution $(')$. Now, since solutions $(')$ and $('')$ have nearly the same compositions and concentrations with regard to the diffusible ions, we may put with sufficient approximation $f'_i = f''_i$.

Therefore, since $\frac{z_i F \psi}{RT}$ is sufficiently small, we may write

$$m'_i = m''_i \left(1 + \frac{z_i F \psi}{RT}\right).$$

Summation over all the (positive and negative) diffusible ionic species gives

$$\Sigma m'_i - \Sigma m''_i = \frac{F\psi}{RT} \cdot \Sigma z_i m''_i,$$

and therefore $\Sigma m'_i = \Sigma m''_i$, since $\Sigma z_i m''_i = 0$. Hence, $\pi = \bar{g}RT \Sigma m'_G$. If $w =$ the mass concentration of the non-diffusible colloidal material per unit volume of water, and $M =$ the mean molar mass of this material, $\Sigma m'_G = w/M$, and we get finally

$$\pi = \bar{g}RT\frac{w}{M}.$$

From this equation $M$ can be calculated if we know $\pi$ and $\bar{g}$. This argument, which the author owes to the kindness of Mr. E. A. Guggenheim, will be sufficient to satisfy the most determined opponent of the " chemical " formulation of colloidal electrolytes, and to demonstrate the generality of the method employed in this paper.

## Summary.

1. The thermodynamic theory of membrane equilibria has been applied to the determination of the osmotic pressures and molar masses of colloidal electrolytes in the following cases : (a) monodisperse singly ionised electrolyte ; (b) monodisperse multiply ionised electrolyte ; (c) monodisperse multiply ionised ampholyte ; (d) polydisperse multiply ionised electrolyte.

2. The same theory has been applied to the determination of the electrovalencies of colloidal ions.

3. It has been shown that the theory is essentially independent of any special formulation of colloidal electrolytes.

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# ON THE APPLICATION OF GIBBS' FUNDAMENTAL EQUATIONS TO PROTEIN SYSTEMS.

## By G. S. ADAIR.

In his work on the equilibrium of heterogeneous substances, Gibbs [1] showed that the chemical, thermal and mechanical properties of a solution are correlated with certain thermodynamical functions termed chemical potentials.   All of these functions can be deduced if the energy, entropy and volume of the solution are known functions of the masses of the components.   An equation of this type, exemplified by formula 2, is termed a fundamental equation.   The number of variables in this equation is $2n + 5$, where $n$ is the number of components of the system, and for the correlation of the potentials with experimental data, it may be necessary to derive less general equations, applicable to systems in which certain variables are kept constant.

Examples of such formulæ, with special reference to experimental conditions favourable for the investigation of protein solutions, are derived below, from the formulæ of Gibbs, who defined the energy, or rather the increment of the energy, $d\epsilon$, of a fluid by the formula $d\epsilon = dH - dW$, where $dH =$ the heat received, $dW =$ the work done by the fluid.   If there be no appreciable changes in electrical or surface energy,[2] $dW =$ the mechanical work $pdv$, where $p =$ the pressure, $v =$ the volume of the fluid and $d\epsilon = td\eta - pdv$;  $t =$ the absolute temperature and $\eta =$ the entropy, which is defined by the formula $d\eta = dH/t$.

If the composition of the fluid be varied, and if $m_1, m_2 \ldots m_n$ be the masses of the components $S_1, S_2 \ldots S_n$, the energy $\epsilon$ is then a function of $m_1, m_2 \ldots m_n$, as expressed in the formula

$$d\epsilon = td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 + \ldots + \mu_n dm_n \qquad . \quad (1)$$

[1] Gibbs, *Trans. Conn. Acad.*, **3**, 108, 1876 ; *Collected Works,* I. *Thermodynamics,* New York, 1928.

[2] Hardy, *Roy. Soc. Proc.*, **86A**, 601, 1912, discusses a colloidal system where surface forces are important.

The terms $\mu_1$, $\mu_2$, $\mu_n$ denote the chemical potentials of $S_1$, $S_2$, $S_n$, defined by formulæ of the type $\mu_1 = (\partial\epsilon/\partial m_1)\eta \cdot v \cdot m$, where the entropy, volume and the masses of the components except $m_1$ are constants. If the molecular weights be known, $m_1$, $m_2 \ldots m_n$ are expressed in gram mols.

The values of the potentials are independent of the mass of the solution, if the proportions of the components be kept constant, and equation (1) is integrated on the assumption that the masses are increased from 0 to $m$.

$$\epsilon = t\eta - pv + \mu_1 m_1 + \mu_2 m_2 + \ldots + \mu_n m_n \quad . \qquad . \quad (2)$$

Formula (2) is differentiated in the most general manner,

$$d\epsilon = td\eta + \eta dt - pdv - vdp + \mu_1 dm_1 + m_1 d\mu_1,$$

and formula (3) is obtained by comparison with 1.

$$0 = \eta dt - vdp + m_1 d\mu_1 + m_2 d\mu_2 + \ldots + m_n d\mu_n \qquad . \quad (3)$$

The activity [3] is correlated with the potential at a constant pressure and temperature by formula (4).

$$\mu_1 = RT \ln a_1 + constant = RT \ln f_1 N_1 + constant \qquad . \quad (4)$$

$a_1$ = activity, $f_1$ = activity coefficient, $N_1$ = molar fraction of the substance $S_1$. In ideal solutions, $f_1$ is equal to unity.

## Conditions for the Application of Gibbs' Equations to Protein Systems.

The most important condition for the application of Gibbs' equations to protein systems is the existence of a stable equilibrium. In the absence of electrolytes, or in the presence of high concentrations of certain electrolytes, proteins may be unstable, but within certain ranges of concentration and at low temperatures, the degree of stability may be sufficient to justify the application of equations that are valid for reversible equilibria.

The number of components in the protein system must be determined by experiment; in mixtures of a protein, water and sodium hydroxide in the range where the protein is stable, the number of components may be three, if the properties of the system be determined by the temperature and pressure, and the concentrations of the three components. The number of different chemical compounds may exceed the number of components, since series of compounds between a protein **Pr** and a crystalloid **X** may be present in equilibrium in the solution. If the composition of the compound be determined and represented by the formula **Pr** $X_n$, the number $n$ represents a mean value, determined by proportions of the series of compounds in formula (5).

$$\mathbf{Pr} + \mathbf{PrX_1} + \mathbf{PrX_2} + \ldots + \mathbf{PrX_n} + \mathbf{PrX_{n+1}} + \mathbf{PrX_{n+2}} + \ldots + \quad (5)$$

The general equations of Gibbs are not invalidated by the existence of series of compounds of this type, but special methods may be required for the estimation of the activity coefficients and the activities of protein salts. The methods described by Lewis and Randall [3] refer to the activities of individual compounds rather than the mean activity of a series.

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[3] Lewis and Randall, *Thermodynamics*, New York, 1923.

## Membrane Equilibrium in Systems Composed of Diffusible Non-Electrolytes and Salts and a Protein Salt.

The stability and the thermodynamical properties of protein salts of approximately constant composition may be investigated by osmotic methods, and if the measurements of osmotic pressure be correlated with determinations of the distribution of diffusible substances across membranes permeable by crystalloids but impermeable by colloids, it is possible to investigate the potentials of all of the components of a protein system. The components can be divided into three groups, diffusible non-electrolytes, diffusible salts and protein salts. The potential $\mu'_n$ of a diffusible non-electrolyte in the protein solution is given by formula (6), if $\mu''_n$, the potential of the non-electrolyte in the dialysate, be known or can be calculated from chemical analyses.

$$\mu'_n = \mu''_n \qquad . \qquad . \qquad . \qquad (6)$$

In all of the formulæ given below, the same notation is used to distinguish between the protein solution and the dialysate; terms with two accents refer to the dialysate.

The potential of a diffusible salt which ionises to yield $\nu_+$ cations and $\nu_-$ anions is given [4,5] by formula (7)

$$(\nu_+\mu'_+ + \nu_-\mu'_-) = (\nu_+\mu''_+ + \nu_-\mu''_-) \qquad . \qquad . \qquad (7)$$

$\mu_+ =$ potential of cation, $\mu_- =$ potential of anion. The potential of the protein salt is obtained by a method suggested in a previous paper.[6] By formula (3), the potential of the protein salt $\mu_{ps}$ in a mixture containing a number of crystalloids is given by the formula $v dp = m_{ps} d\mu_{ps}$ if $dt$, $d\mu_1$, $d\mu_2 \ldots d\mu_n$ be equal to zero. By formulæ (6) and (7), $\mu'_1$, $\mu'_2$, $\mu'_n$ are the same on both sides of the membrane, and if the protein solution be equilibrated with relatively large volumes of dialysate of constant temperature, pressure and composition, $\mu_{ps}$ is determined by formula (8),

$$\mu'_{ps} + I_1 = \int V dp = \int V \left(\frac{\partial p}{\partial c_p}\right)_\mu dc_p \qquad . \qquad . \qquad (8)$$

$\mu'_{ps} =$ potential of a protein salt at the osmotic equilibrium pressure, $I_1 =$ an integration constant, $V =$ volume of solution per g. mol. protein, $p =$ osmotic pressure measured by a membrane permeable by crystalloids, $c_p =$ g. mols. protein salt per litre of solution. The molar concentrations of the protein salt and of the protein ions are identical. The subscript $\mu$ denotes that the potentials of crystalloids are constant. Since the effect of hydrostatic pressure is determined by the formula $\partial \mu_{ps}/\partial p = \bar{v}_p$, where $\bar{v}_p$ is the partial molal volume, the potential at a pressure of one atmosphere is given by formula (9)

$$\mu_{ps} + I_1 = \int (V - \bar{v}_p) dp = \int v_s dp \qquad . \qquad . \qquad (9)$$

$v_s =$ litres of solvent per mol. protein. In practical applications of this formula, protein hydrate rather than dry protein is regarded as a component of the system. If 1 g. dry hæmoglobin of specific volume 0·75

[4] Aqueous solutions of colloidal electrolytes are discussed by Linderstrøm-Lang, *Comptes Rend. lab. Carlsberg*, **16**, No. 6, 1926.

[5] *Cf.* Donnan and Guggenheim, *Z. physikal. Chem.*, **162**, 346, 1932 ; Adair *Science*, **58**, 13, 1923.

[6] Adair, *J. Amer. Chem. Soc.*, **51**, 696, 1929.

can combine with 0·21 g. water,[7] the molecular weight of the hydrate is 67,000 × 1·21 = 81,000, the density is estimated as 1·26 and the molal volume $\bar{v}_p$ as 64·3 litres, a value in agreement with the estimate of 65 litres, based on chloride distribution measurements.[8] A lower value 61·3 litres has been estimated from density and hydration of hæmoglobin crystals suspended in mixtures of saturated ammonium sulphate and sucrose, a medium that has a relatively low vapour pressure.

The correlation of formula (9) with experimental data is facilitated by the definition of two new functions $g_{ps}$ and $f_{ps}$ given by formulæ (10) and (11). There is a formal resemblance between $g_{ps}$ and the osmotic coefficient $\phi$ defined by Bjerrum,[9] in that $\phi$ and $g_{ps}$ both approach unity in dilute solutions, but $\phi$ refers to osmotic pressures $p_w$, given by membranes permeable by water alone, and is defined by the formula $p_w = v\phi RTm$, where $v$ is the number of ions given off by the salt and $m$ is the molality.

$$p = g_{ps} RT\, m_p \qquad . \qquad . \qquad . \qquad . \quad (10)$$

$p$ = pressure measured with a collodion membrane in systems where the potentials of the crystalloids are kept constant.  $m_p$ = g. mols. protein per litre of solvent in the protein solution.  The pressure measured under these conditions is quite different from $p_w$, on account of the unequal distribution of ions across the membrane, described by Donnan.[10]

The functions $a_{ps}$ and $f_{ps}$ are defined by formulæ (11), of the type given by Lewis and Randall in their definitions of activities and activity coefficients.

$$d\mu_{ps} = RT d \ln a_{ps} = RT d \ln f_{ps} m_p = v_s dp \quad . \qquad . \quad (11)$$

In this formula $dp = (\partial p/\partial m_p)_\mu dm_p$.  By combining formulæ (9), (10) and (11) the following expression is obtained

$$\ln f_{ps} = \ln \frac{a_{ps}}{m_p} = (g_{ps} - 1) + \int_0^{m_p} \left( \frac{g_{ps} - 1}{m_p} \right) dm_p \qquad . \quad (12)$$

In the present investigation, it has been found that the observed osmotic pressure may be represented by the empirical formula $p = RT(m_p + km_p^2)$ over a considerable range of concentrations and within this range, $(g_{ps} - 1) = km_p$ and $\ln f_{ps} = 2km_p = 2(g_{ps} - 1)$.

### Membrane Equilibria in Systems Composed of Diffusible Non-Electrolytes, Diffusible Ions and Protein Ions.

The relationship between $a_{ps}$ and $f_{ps}$ and the activities defined by Lewis and Randall has been established by the application of formula (3) to a system where the individual ions are treated as the components of the system, and the composition of the dialysate is kept constant. The potential $\mu_i$ for any diffusible ion of valence $n_i$ is determined by formula (13),

$$\mu_i' = \mu_i'' - n_i FE \qquad . \qquad . \qquad . \quad (13)$$

$F$ = Faraday's constant, $E$ = potential difference across the membrane in volts.  An approximate determination of $E$ is made by measurements

[7] Adair and Robinson, *J. Physiol.*, **72**, 2P, 1931.
[8] Adair, *Roy. Soc. Proc., A*, **120**, 573, 1928.
[9] Bjerrum, *Z. physikal. Chem.*, **104**, 406, 1923.
[10] Donnan, *Z. Electrochem.*, **17**, 572, 1911.

with saturated KCl-calomel electrodes, neglecting liquid junction potentials. If $\mu_i''$ be constant, $d\mu_i' = -n_iFdE$, and by substitution in formula (3),

$$\int v\left(\frac{\partial p}{\partial c_p}\right)_\mu dc_p = m_pd\mu_p' - \Sigma m_i'n_iFdE = m_pd\mu_p' + m_pn_pFdE \ . \quad (14)$$

$\mu_p' =$ potential of the protein ions.  $-\Sigma c_i'n_i$ the sum of the equivalent concentrations of diffusible ions must be equal to $c_pn_p$, where $n_p =$ the mean valence of the protein ions.[11]  The potential of the protein ions at a pressure of one atmosphere is then determined by formula (15),

$$\mu_p + I_2 = \int v_s dp - \int n_pFdE \qquad . \qquad . \quad (15)$$

It has been shown [11] that $n_p$ is constant over a considerable range of protein concentrations, and within this range

$$\int_0^E n_pFdE = e^{nu} = \text{antilog } [n_pE/0{\cdot}05416] \quad . \qquad . \quad (16)$$

$e = 2{\cdot}718$, $u = E \times F/RT$, $n = n_p =$ valence of protein ion; the constant $0{\cdot}05416$ refers to potentials at $0°$.

$$f_{ps} = f_pe^{nu} \qquad . \qquad . \qquad . \qquad . \quad (17)$$

$f_p =$ the activity coefficient of the protein ions, defined by the convention that $f_p$ is unity in very dilute solutions of the protein equilibrated with a dialysate of constant composition.  This function is proportional to the activity $(a_p)_{H_2O}$ defined by Lewis and Randall.

$$(a_p)_{H_2O} = \gamma_p m_p = m_p f_o f_p \qquad . \qquad . \qquad . \quad (18)$$

$(a_p)_{H_2O}$ and $\gamma_p$ denote the activity and the activity coefficient of the protein ion, defined by the convention that $\gamma_p$ equals unity in very dilute solutions free from diffusible salts.  $\gamma_p$ is the product of two functions, $f_0$ and $f_p$, where $f_p$ is a function of the protein concentration and $f_0$ is a constant, when the composition of the dialysate is constant.  In the case of a protein chloride, of valence $n$, $(a_{ps})_{H_2O}$ must be equal to $(a_p)_{H_2O}a_{Cl}^n$, and by formulæ (13), (17) and (18)

$$(a_{ps})_{H_2O} = (m_p f_0 f_p)(a_{Cl}')^n = (m_p f_0 f_{ps})(a_{Cl}'')^n \qquad . \quad (19)$$

## Membrane Equilibrium in Systems where the Molality of the Protein is Constant and the Composition of the Dialysate is Varied.

Under certain conditions, discussed below, it is possible to estimate the value of $f_0$ from measurements of the concentrations of crystalloids in the protein solution and the dialysate, by the application of formulæ (20)-(29), which can be derived from Gibbs' equation (formula 3) by the following method : the potential of water, $\mu_1$ in the protein solution and the dialysate is given by formulæ (29) and (21) if the pressure and temperature in both phases be constant.

$$- m_1''d\mu_1' = m_p'd\mu_{ps}' + m_2'd\mu_2' + m_3'd\mu_3' + \ldots + m_n'd\mu_n' \ . \quad (20)$$
$$- m_1''d\mu_1'' = \qquad\qquad m_2''d\mu_2'' + m_3''d\mu_3'' + \ldots + m_n''d\mu_n'' \quad (21)$$

By formulæ (6) and (7), the potentials are the same in both phases, and if the masses of the phases are such that $m_1' = m_1'' = 55{\cdot}51$ mols. $= 1000$ g.

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[11] Adair and Adair, *Biochem. J.*, 28, 199, 1934.

$H_2O$, the masses of the components in both phases are the same as their molalities. Since $m_1'd\mu_1'$ is then equal to $m_1''d\mu_1''$

$$0 = m_p'd\mu_{ps}' + (m_2' - m_2'')d\mu_2' + (m_3' - m_3'')d\mu_3' + \ldots + (m_n' - m_n'')d\mu_n' \quad (22)$$

$m_2' - m_2''$ represents the excess of the component $S_2$ in the protein solution. Let $\Delta_2 =$ the excess per mol. of protein $= (m_2' - m_2'')/m_p$. It follows that if the measurements of $\Delta_2$ be made in a range where the observed osmotic pressure is independent of the potentials of the crystalloids

$$- d\mu_{ps} = \Delta_2 d\mu_2 + \Delta_3 d\mu_3 + \ldots + \Delta_n d\mu_n \quad . \quad . \quad (23)$$

$$- d \ln f_0 = \Delta_2 d \ln a_2 + \Delta_3 d \ln a_3 + \ldots + \Delta_n d \ln a_n \quad . \quad (24)$$

If the osmotic pressure be a function of the concentration of the crystalloids,[12, 13]

$$d\mu_p' = \left(\frac{V_1}{m_p}\right)dp - \Delta_2 d\mu_2 - \Delta_3\, d\mu_3 - \Delta_n d\mu_n \quad . \quad . \quad (25)$$

$$d \ln f_0 f_p = dg_{ps} - \Delta_2 d \ln a_2 - \Delta_3 d \ln a_3 - \Delta_n d \ln a_n \quad . \quad (26)$$

$V_1 =$ volume of a solution containing 1000 g. water, $g_{ps} =$ the osmotic coefficient in formula (10). Formula (26) is an approximate form of (25) applicable to systems where the concentrations of crystalloids are low and the changes in pressure are small.

Formula (27) is obtained if the individual ions be considered as the components of the system

$$m_p d\mu_p = V_1 dp - m_p n_p F dE - \Sigma(m_i' - m_i'')d\mu_i'' \quad . \quad (27)$$

In the special case where the dialysate contains two univalent ions and $E$ is very small, the approximate formula (28) is obtained.

$$d \ln f_0 = b_+ d \ln a_+'' + b_- d \ln a_-'' \quad . \quad . \quad . \quad (28)$$

$b^+$ and $b^- =$ the excess of the ions $S_+$ and $S_-$, calculated by formula 29

$$m_+' - m_+'' e^{-u} = b_+ m_p \quad . \quad . \quad . \quad (29)$$

The conditions for the application of formulæ (23) to (28) can be shown by the following examples : (1) If the terms $\Delta_2$, $\Delta_3$ and also $b^+$ and $b^-$ are all equal to zero, it may be inferred that $f_0$ is equal to unity. (2) If $\Delta_2$ be positive and attributable to interionic forces rather than chemical combination, $f_0$ is diminished by an increase in $d \ln a_2''$. (3) If $\Delta_2$ be positive and attributable to a simple mass action equilibrium as shown in the formula $[\mathbf{Pr}][\mathbf{X}]^n = k[\mathbf{PrX}_n]$, the value of $f_0$ calculated by formula (24) represents the fraction of the total protein uncombined with the crystalloid. (4) If $\Delta_2$ be positive and attributable to a generalised mass action equilibrium of the type shown in formula (5), the function $f_0$ calculated by formulæ (24) and (26) has no simple physical significance.

[12] Cf. Christiansen, Comptes Rend. lab. Carlsberg, 17, No. 6, 1928.

[13] Failey, J. Physic. Chem., 37, 1075, 1933, derived a special form of (26) by a different method, applicable to isoelectric protein in a system containing water and one salt. He applies the law of mass action $a_1^n a_3 = a_4 = constant$, where $a_1$ $a_3$ and $a_4$ denote activities of water, protein and protein hydrate, and $n =$ number of mols. of water combined. Adair, J. Biol. Chem., 63, 493, 499 and 529, 1925, discussed reactions which do not obey the law of constant proportions, and chemical equilibria where series of compounds are formed, and obtained a formula different from the mass action equation used by Failey.

The experiments recorded in Table I. show that when hæmoglobin is equilibrated with dilute solutions of the ammonium phosphates $(NH_4)_2HPO_4$ and $NH_4H_2PO_4$ in which approximately half of the total phosphate is present in the bivalent form, the molalities of anions and of cations is greater in the protein solution than in the dialysate. The excess $(b^-)$ calculated by a modification [11] of formula (29) is much greater

TABLE I.—MEMBRANE EQUILIBRIUM OF SHEEP CO HÆMOGLOBIN AND AMMONIUM PHOSPHATES AT 0°.

| | | | | |
|---|---|---|---|---|
| [Hæmoglobin], mols. per 1000 g. $H_2O$ . . . . . | 0·00407 | 0·00403 | 0·00407 | 0·00415 |
| [Phosphate] in protein solution | 0·01320 | 0·02180 | 0·03410 | 0·05550 |
| [Phosphate] in dialysate . . | 0·00496 | 0·00996 | 0·02010 | 0·03440 |
| [Ammonium] in protein solution | 0·00890 | 0·01620 | 0·03510 | 0·05410 |
| [Ammonium] in dialysate | 0·00761 | 0·01510 | 0·02990 | 0·05150 |
| Excess $PO_4$ mols. per mol. Hb $(b_-)$ | 1·8 | 2·8 | 3·8 | 5·4 |
| Excess $NH_4$ mols. per mol. Hb $(b_+)$ | 0·5 | 0·4 | 0·9 | 0·3 |
| Valence of protein ion . . | + 0·5 | + 0·3 | − 0·4 | − 1·0 |
| Acid combined [hydrogen ions] | + 2·9 | + 4·2 | + 4·4 | + 6·9 |
| $p_H$ of protein solution . . | 7·15 | 7·10 | 7·02 | 6·95 |
| Membrane potential in mv. . | + 2·47 | + 0·68 | − 0·47 | − 0·69 |
| Isoelectric point . . . | 7·32 | 7·18 | 6·92 | 6·71 |
| Osmotic coefficient $g_{ps}$ . . | 1·68 | 1·61 | 1·56 | 1·55 |
| $f_{ps}$ (approx.) . . . | 3·90 | 3·39 | 3·06 | 3·01 |
| $f_p$ (approx.) . . . . | 3·72 | 3·36 | 3·04 | 2·93 |

for the anions than for the cations, and increases with the phosphate concentration. The electrometric measurements indicate that the excess of $NH_4$ and $PO_4$ inside the membrane is not entirely due to interionic forces, since the salts alter the valence of the protein and its isoelectric point.[14] The measurements of the distribution of salts are consistent with the formation of a series of compounds (formula 5) and in the circumstances, the estimation of $f_0$ must be deferred.

## Molecular Weights of Proteins in the Presence of Salts.

In the ultracentrifugal and osmotic methods for the determination of the molecular weights of proteins, diffusible salts are added in order to eliminate the effects of ions predicted by Donnan's theory [10] of membrane equilibrium. The arguments usually advanced in favour of this procedure are not satisfactory; since the pressure $p_i$ due to the excess of diffusible ions is given by formula (30), it is evident that as the salt concentration is increased, the effects of small difference between the osmotic coefficients might be increased by the addition of salts.

$$p_i = RT(g'_{Na}[Na]' + g'_{Cl}[Cl]' - g''_{Na}[Na]'' - g''_{Cl}[Cl]'') \qquad . \quad (30)$$

The calculation of $p_i$ by the application of Gibbs' methods has been described in a previous paper,[15] in which formula (31) was obtained.

$$p_i = RT\int_0^u m_p n_p du = RT\int_0^u m_p n_p \left(\frac{\partial u}{\partial m_p}\right)_\mu dm_p \qquad . \quad (31)$$

$m_p n_p$ = the " corrected " equivalent concentration of the protein in g. equivalents per litre of solvent or dispersion medium in the protein solution. The symbol $\mu$ refers to the potentials of the diffusible components

[14] Adair and Adair, *Biochem. J.*, **28**, 1230, 1934, *cf.* refs. (8) and (11).
[15] Adair, *Roy. Soc. Proc.*, **126A**, 16, 1929.

in the dialysate.   Formula (31) is applicable to systems where the dialy-
sate may be a mixture of diffusible ions of different valences.   A com-
parison of values of $p_i$ calculated by this formula and by other methods
has been made by Adair and Robinson.[16]

It is necessary moreover to consider the effects of salts on the partial
pressures of the protein ions themselves.   The formulæ (24) and (26)
show that although the addition of diffusible salts may cause relatively
large changes in the activities of the protein ions, the calculation of the
molecular weights by the application of van't Hoff's law is not necessarily
invalidated, because the change in the activity of the protein ions may
be correlated with a non-ideal distribution of salts across the membrane,
rather than an abnormal osmotic pressure.

## Hydration of Proteins.

Sørensen [17] has discussed the estimation of the water bound by egg-
albumin.   If the distribution of a salt $S_2$ across the membrane be un-
affected by chemical combination or by interionic forces, and if a small
correction for the effects of hydrostatic pressure can be neglected, the
ratio $m_2/m_1$ should be the same on both sides of the membrane, and if
the observed mass of water $m_1'$ in the protein phase exceed the calculated
value, the excess is attributable to hydration.   Assuming that the value
of $f_0$ can be estimated from measurements of solubility, formula (24)
can be applied to determine the most favourable conditions for the
estimation of hydration.

As a general rule, small amounts of salts increase the solubility of
proteins; $\partial \ln f_0 / \partial \ln a_2$ is then negative, $\Delta_2$ is positive and the bound
water is under-estimated.   Concentrated solutions of salts, including
ammonium sulphate, usually reduce the solubility; $\partial \ln f_0 / \partial \ln a$ is
then positive, $\Delta_2$ is negative and the water is overestimated.   At the
point of inflection, $\partial \ln f_0 / \partial \ln a_2$ is equal to zero, $\Delta_2$ is equal to zero and
the estimation of the bound water is exact.   These conclusions may
require qualification if the substance $S_2$ be present in the solid phase, or
if a series of compounds be formed, as indicated in formula (5).

## Distribution of a Protein in Gravitational or Centrifugal Fields.

Gibbs [1] showed that the potentials of the components in a gravi-
tational field are determined by a series of equations of the form
$\mu_1/M_1 + \phi_g h = $ constant.   $M_1 = $ molecular weight, $h = $ the height and
$\phi_g = $ the force of gravity.   Tiselius [18] has discussed the equilibrium of
a colloid in a centrifugal field, using the activity notation, with special
reference to systems of two components.   A complete analysis of the
problem in the case of systems of three or more components has not been
published, although an approximate formula has been obtained by
Svedberg.[19]   A more rigorous solution may be given by the following
procedure.

Let $p'$ be the hydrostatic pressure at a point $y$ cm. below the surface
of a protein solution ; let $p''$ be the hydrostatic pressure at a point $y$ cm.
below the surface of a dialysate, separated from the protein solution by
a membrane permeable by all of the crystalloids present in the solution ;

[16] Adair and Robinson, *Biochem. J.*, **24**, 1864, 1930.
[17] Sørensen, *Comptes Rend. lab. Carlsberg*, **12**, 1917.
[18] Tiselius, *Z. physikal. Chem.*, **124**, 449, 1926.
[19] Svedberg, *Kolloid Z.*, **67**, 1, 1934.

let $p' - p'' = p$, where $p =$ the osmotic pressure. If the densities of the colloidal solution and of the dialysate be equal to $D'$ and $D''$, $dp$ is equal to $(D' - D'')dy$.

Measurements [20] of the densities of protein solutions equilibrated with a dialysate of constant composition show that $D' - D'' = k_d x = k_d M . 10^{-3} c_p$, where $k_d =$ an empirical constant, $x =$ g. dry protein per ml. solution and $M =$ molecular weight in g. dry protein.

Let $g^*$ and $f^*$ be defined by the formulæ (32) and (33):

$$p = RT g^* c_p \qquad . \qquad . \qquad . \qquad (32).$$

$g^*$ differs from $g_{ps}$ defined by formula (10), since $c_p$ is expressed in g. mols. per litre of solution.

$$RT \, d \ln f^* \, c_p = V \, dp = V \, (\partial p / \partial c_p)_\mu \, dc_p \quad . \qquad . \quad (33).$$

If pressures be expressed in cms. of fluid of density 1·0:

$$\frac{1}{c_p} \, dg^* c_p = d \ln f^* c_p = k_d 10^{-3} \, M . (RT)^{-1} \, dy \quad . \qquad . \quad (34).$$

Formula (34) differs from Svedberg's equation in two respects ; firstly it includes the functions $g^*$ and $f^*$. Since the ultracentrifugal measurements are made with very dilute solutions, it is probable that both $g^*$ and $f^*$ approach unity. Secondly, the empirical constant $k_d$ replaces the expression $(1 - v_a \rho)$ in his formula, where $\rho$ is the density of the solvent and $v_a$ is the specific volume of the dry protein. In aqueous solutions, $k_d$ and $(1 - v_a \rho)$ must be equal, but in mixtures of three components, $k_d$ is not necessarily equal to $(1 - v_a \rho)$, if the protein can combine with water or with crystalloids. Experimental investigations which will be published later show that in the case of dilute salt solutions in the region of the isoelectric point, $k_d$ and $(1 - v_a \rho)$ are approximately equal. If the dialysate be a dilute acid or base, $k_d$ may be relatively high, on account of the excess of ions inside the membrane. If the salt concentration be high, the effects of hydration are important and $k_d$ is relatively low.

## Summary.

The methods of Gibbs are adapted for the thermodynamical treatment of systems of many components, including a protein salt which may exist in the form of a series of salts of different valence. The theory of membrane equilibrium has been extended to determine the activities of all of the components of such a system, and reference has been made to the determination of molecular weights, hydration, reactions which do not obey the law of constant proportions and to the equilibrium of a protein in gravitational or centrifugal fields of force.

*From the Physiological Laboratory,*
*Cambridge.*

## GENERAL DISCUSSION.*

**Mr. G. S. Hartley** (*London*) said that he thought there was an error in the approximations used by Professor Donnan in his deduction of the osmotic pressure in the " swamped " case, the correction of which would make the formula for this quantity even more simple than the

[20] Roche, Roche, Adair and Adair, *Biochem. J.*, **26**, 1811, 1932.
* On the two previous papers.

one given. The slight difference in activity coefficient of NaCl in the solutions on opposite sides of the membrane was neglected in writing equation (7) and this amounted to neglect of a term inside the bracket of equation (8) which was probably comparable with $m'_{G+}(1 - g')$. The speaker thought that the effect of this might be to compensate exactly for the difference of the $g$'s from unity so that equation (9) might become simply $\pi = RTm'_{G+}$. He had found this to be true for a special case which he then dealt with, and he thought that the argument could probably be generalised although he had not yet attempted to do so.

Suppose we have two identical solutions of a uniunivalent electrolyte at concentration $C$, assumed sufficiently small for the osmotic and activity coefficients, $g$ and $f$, of the salt to be related sufficiently exactly by the equation

$$\frac{d(gC)}{dC} = \frac{d \log (fC)}{d \log C}. \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

Let these solutions be separated from water by membranes impermeable to all ions. Now let another electrolyte be added to one of these solutions in concentration $\delta_1 C$ small compared with $C$, this electrolyte being identical with the first except that both its ions are impermeant to a second membrane through which the solutions may be connected and which is permeable to the ions of the first electrolyte. Before connecting the two solutions through the second membrane their osmotic pressures against pure water will differ by a quantity

$$2RT\delta_1(gC) = 2RT(g\delta_1 C + C\delta_1 g). \qquad . \qquad . \qquad . \qquad (2)$$

$C\delta_1 g$ is not in general negligible compared with $(1 - g)\delta_1 C$ as can be seen if we consider $g$ to decrease linearly with $\sqrt{C}$ as it will in very dilute solutions. In this case

$$C\delta_1 g = -\frac{(1 - g)}{2} . \delta_1 C.$$

When the solutions are connected through the second membrane, the difference of osmotic pressures, and hence the osmotic pressure of one solution against the other will not be given by (2) because of a significant slight increase in the concentration of the first electrolyte on the side of the membrane containing the second. If we assume that the volume of solution on the first side of the membrane is infinite, its concentration will be unchanged. Let the increase of concentration of the diffusing electrolyte on the other side be $\delta_2 C$, and let the operator $\delta$ denote an increment of a quantity due to both $\delta_1 C$ and $\delta_2 C$ (remembering that the electrolytes are identical except in permeability). The equilibrium of the diffusible electrolyte is determined by

$$C . f = (C + \delta_2 C)(f + \delta f) \qquad . \qquad . \qquad . \qquad (3)$$

whence, neglecting second powers of $\delta$'s, we have

$$\delta_2 C = -C\delta \log f \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

The difference of osmotic pressures of the solutions against water and hence the osmotic pressure of the one with respect to the other, will be

$$\delta\pi = 2RT\delta \ (gC) \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (5)$$

which, by (1)         $= 2RTC\delta \ \log (fc)$

or                   $= 2RT \ (\delta C + C\delta \log f)$

which, by (4)       $= 2RT \ (\delta C - \delta_2 C)$

or                   $= 2RT\delta_1 C,$

whence we conclude that the relevant osmotic coefficient is unity.

**Professor F. G. Donnan** (*London*) said : I am much obliged to Mr. G. S. Hartley for his remarks. I think that his criticism is justified, and will hold good for all the cases discussed in my paper. If so, a very valuable simplification is effected, for the factor $\bar{g}$ will disappear from all the final equations. I hope to have the opportunity of returning to this interesting and important matter in a future publication.

**Dr. Andrée Roche** (*Marseilles*) said : In his paper, Dr. Adair gave a formula correlating the osmotic pressure to the equilibrium in a centrifugal field. The two methods for the determination of the molecular weight of proteins based on these two kinds of datas, namely his own method, and Svedberg's ultracentrifugal method, have always given very consistent values except for serum globulin. Svedberg and Sjögren found for horse serum total globulin 103,000, whereas Adair and Robinson gave 175,000. More recently Mutzenbecher, using Svedberg's method, found 140,000. It seemed worth while to try to explain these differences.

Mr. Bracco and myself, using Dr. Adair's method, found 150,000 for the molecular weight of horse total globulin prepared from fresh serum, a value which is in good agreement with Mutzenbecher's. We were able moreover to explain the discrepancy between this data (140,000-150,000) and the higher one (175,000) given by Adair and Robinson. These authors prepared the globulin from a bacteriological serum which had been previously heated. During this process, part of the lipoid-globulin complex is split off, and lipoids are precipitated. Some experiments made by us with globulin prepared after this change has occurred, gave a molecular weight of 200,000. This increase is very likely to be attributed to aggregating processes taking place by means of co-ordinative valencies which may be liberated by the breaking down of part of the complex. The high molecular weight found by Adair and Robinson is thus explained.

The mean molecular weight of horse serum total globulin prepared from freshly collected serum is therefore to be taken as 140,000 to 150,000. Higher values being obtained when the serum has been previously heated as it is usually done in bacteriological departments.

The disagreements between the two methods for serum globulin is therefore explained by the datas brought by our experiments.

**Dr. G. S. Adair** (*Cambridge*) said : The observations of the osmotic pressure of globulin made by Dr. A. Roche are of great interest in throwing light on the discrepancies between earlier measurements of molecular weights of proteins by osmotic and by ultra centrifugal methods. Unpublished observations of the density of globulin solutions and of their dialysates show that these discrepancies cannot be accounted for by the difference between the formula 34 given above and the equation used by Svedberg. It seems probable that the size of the particles of globulin may be affected by slight differences in the methods of preparation.

Dr. J. A. Christiansen kindly wrote to me, drawing my attention to an oversight in the discussion of the potentials of the proteins in a previous paper,[1] where it is assumed, but not stated explicitly, that the symbol $\mu_{ps}$ refers to potentials at a pressure of one atmosphere, and $(\mu_{ps})_\mu$ refers to potentials at a pressure of one atmosphere plus the osmotic equilibrium pressure.

In his paper on the determination of the molecular weights of colloids, Professor Donnan has pointed out that the osmotic coefficient of

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[1] *J. Amer. Chem. Soc.*, **51**, 696, 1929. Formula 4.

the colloidal ions may differ from unity, and he has suggested a method for attacking this difficulty. An alternative method of treatment shows that even in non-ideal solutions, there are certain conditions, specified below, under which the partial pressure of the colloidal ions $(p_p)$ may be determined by the simple formula $p_p = RT m_p$, where $m_p = g$. mols. of colloid per litre of solvent, which includes not only water but also the diffusible substances present in the mixture. If $a$, the activity of the colloidal ions be equal to $m_p f_0$, where $f_0$ is a function of the salt concentration, but independent of $m_p$, and if activities and osmotic pressures be correlated by a generalised form of the equations for simple aqueous solutions,[2] modified by the condition that the composition of the dialysate be a constant, $RT$ d ln $a = v_s$ d $p_p$, where $v_s = 1/m_p$, and it follows that $RT m_p = p_p$, within the range where $f_0$ is a constant and d ln $a$ is equal to d ln $m_p$.

In experimental determinations of molecular weights, it is necessary to allow for the pressure $p_i$, due to the excess of diffusible ions inside the membrane. In the first application of Donnan's theory, due to Sørensen, a very high concentration of salts is used to eliminate $p_i$. In the second method,[3] the limiting value of the pressure concentration ratio is determined by extrapolation.

In the second method, the conditions are favourable not only for the elimination of $p_i$, but also for the elimination of deviations from the ideal solution laws.

**Dr. A. Wassermann** (*London*) said : The increase in solubility of proteins in salt-solutions of low concentrations might be related to the formation of undissociated protein-salts. The intermolecular forces of a " true " protein-salt might be smaller than those of a *Zwitterion*, whereby the increase in solubility would be explained. The cause of the formation of undissociated protein-salts is to be sought in the high polarisability of the molecules under consideration. The polarisability of organic molecules is responsible for the fact that solid alkali salts of carboxylic acids crystallise in molecule lattices.

**Dr. O. S. Adair,** in reply, said : Dr. Wassermann's suggestion that proteins form unionised compounds is in accordance with experiments on the equilibria of protein crystals, solutions and dialysates, which indicate that in the region of the isoelectric point, haemoglobin crystals contain combined ammonium or phosphate ions.[4] Since the solubilities are affected by the sum of the effects of interionic forces and chemical combination, further investigations are required to estimate the changes in solubility due to different factors.

[2] More detailed investigations bearing on this problem are given in the references numbered 6 and 15, given above.

[3] Adair, *Proc. Camb. Phil. Soc.* (*Biol.*), **1,** 75, 1924 ; *Proc. Roy. Soc.*, **120A** 573, 1928.

[4] *Biochem. J.*, **28,** 1230, 1934.

# A NEW DETERMINATION OF THE CAPACITY OF THE ELECTRICAL DOUBLE LAYER.

By M. Proskurnin and A. Frumkin.

*Received 17th July, 1934.*

The capacity of the electrical double layer is very important for every quantitative theory of the distribution of ions around a solid particle, but up to the present there has been a rather puzzling discrepancy between various estimations of this quantity. In the case of a mercury electrode the capacity can be calculated by means of the Lippman-Helmholtz equation from surface tension data. Calculations of this kind have been carried out with a high degree of accuracy by Gouy.[1] They give a minimum value of ca. 17 $\mu F/cm.^2$ in the region of the descending branch of the electrocapillary curve, *i.e.*, at considerable cathodic polarisations. We owe the first reliable direct determination to Krüger,[2] who made his observations with a cathodically polarised surface, using alternating current and obtained values between 7 and 10 $\mu F/cm.^2$. In a later paper[3] Krüger and Krumreich considered 13 $\mu F/cm.^2$ as the most probable value for a potassium nitrate solution. More recently, Bowden and Rideal[4] found that in the region of hydrogen overvoltage $6 \times 10^{-7}$ coulombs per square centimetre caused a change of 100 millivolts in the electrode potential at a mercury surface in sulphuric acid. The capacity of the double layer should be therefore only 6 $\mu F/cm.^2$. Erdey Gruz and Kromrey[5] made extensive measurements with different electrolytes and compared the experimental results with the values calculated by Gouy. As a rule, the observed values were much too low, in the case of normal sulphuric acid the minimum value being, for instance, only 3 to 6 $\mu F/cm.^2$. The discrepancy between the electrocapillary data and the measured values of the capacity attracted the attention of many authors, but no adequate explanation has been proposed until now. This fact was especially striking, as measurements of the electric charge per unit surface, carried out by expanding the mercury surface at constant potential,[6] gave values in fair agreement with the theory of electrocapillarity. It seemed therefore advisable to take up this question once more.

The experimental procedure will be described in detail elsewhere; in this paper we mention only the most important features.

The solution was carefully saturated with hydrogen and freed before the measurements from the last traces of oxygen and mercury ions by electrolysis. The apparatus was made exclusively of glass, the ground joints being wetted only with water, without any lubricants. In order to lessen the errors caused by contamination and by the creeping of the solution between the mercury and the glass, the experiments were made with a rather large mercury surface of 5·1 cm.² This was formed in a glass cup, which could be filled with mercury from underneath through

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[1] *Ann. chim. physique*, (7), **29**, 159, 1903.
[2] *Z. physik. Chem.*, **45**, 1, 1903.   [3] *Z. Elektrochem.*, **19**, 620, 1913.
[4] *Proc. Roy. Soc.*, 120A, 59, 1928.   [5] *Z. physik. Chem.*, **157A**, 213, 1931.
[6] Frumkin, *Z. physik. Chem.*, **103**, 55, 1922 ; Philpot, *Phil. Mag.*, 775, 1932.

a glass tube. To clean the surface the mercury was allowed to overflow the borders of the cup. In order to maintain a definite potential at the surface, the latter was polarised with the help of an auxiliary anode with direct current and its potential measured against a non-polarisable electrode separated from the cell by a siphon.

To determine the capacity, the mercury surface was polarised with an alternating current of 50 periods with the help of a second auxiliary electrode situated above the mercury surface. The variations of the potential
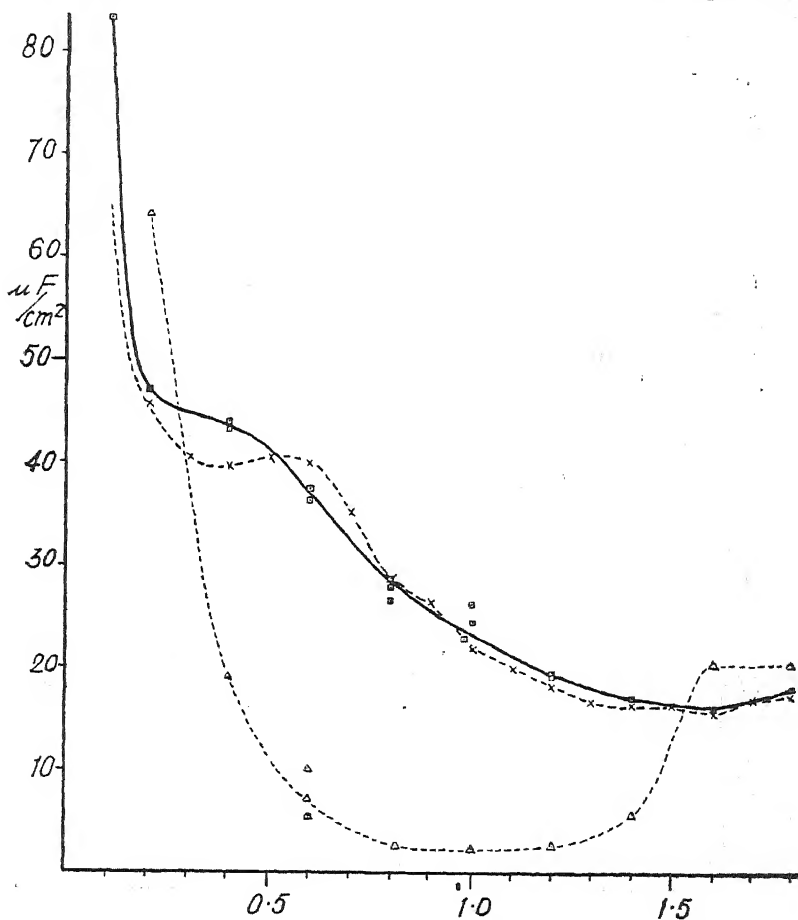


Norm. $Na_2SO_4$. ☐ Observed values, clean surface. △ After contamination with picein. × Calculated from electrocapillary curve.

FIG. 1.

difference between the mercury and a reference electrode (platinum ring round the cup on a lower level than the mercury surface) were amplified about 3000 times with a two tube amplifier and measured with a cathodic oscillograph. To check the value of the capacity we used a standard capacity equal to 8·92 $\mu F$. The amplitude of the potential oscillations as a rule did not exceed 15 millivolts. A special filter practically prevented the alternating current from entering the circuit formed by the mercury cathode and the auxiliary anode.

Measurements have been carried out with normal solutions of $Na_2SO_4$, KCl, NaOH, $H_2SO_4$ and $Na_2SO_4$ saturated with octyl alcohol, and the values of the capacity plotted against the cathodic polarisation. The zero point on the potential scale corresponds to the saturation of the solution with the respective mercury salt, *i.e.*, $Hg_2SO_4$ in $Na_2SO_4$ and $H_2SO_4$, HgO in NaOH and $Hg_2Cl_2$ in KCl.

**Sodium Sulphate** (Fig. 1). The salt was heated to 550° in a platinum crucible and dissolved in twice distilled water. The capacity was inde-
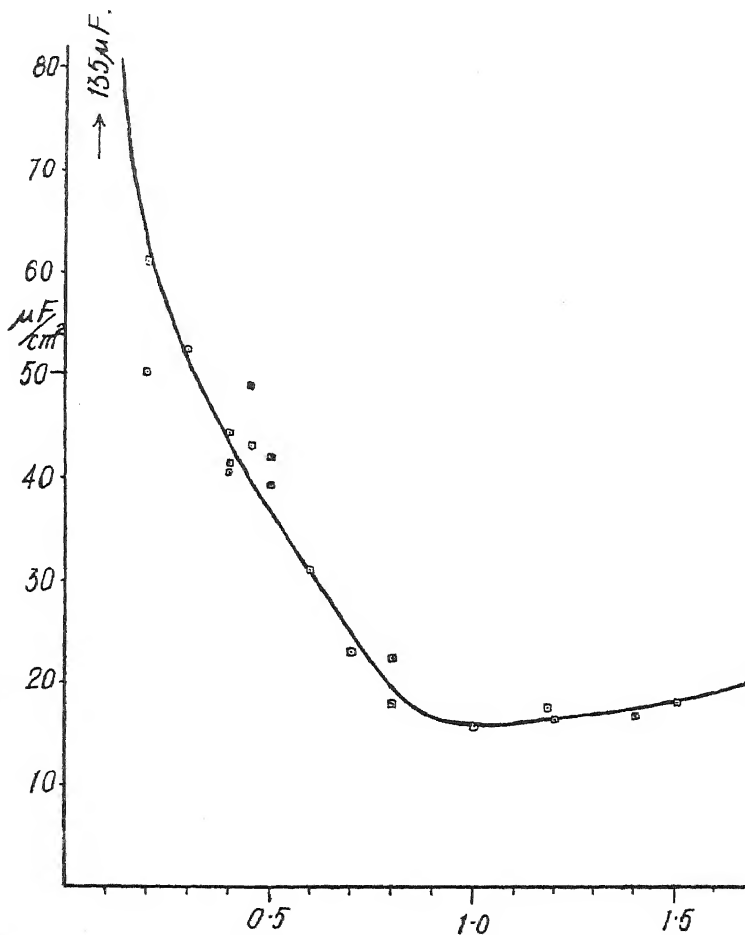


Norm. KCL. Observed values.
FIG. 2.

pendent of the age of the surface. The agreement with the values calculated by Gouy is quite satisfactory, especially on the descending branch of the electrocapillary curve, the minimum being 16·5 $\mu F/cm.^2$. The value of the capacity is very sensitive to surface contamination : touching the surface with a picein stick caused, as shown by Fig. 1, an enormous decrease of the capacity in the middle part of the curve.

**Potassium Chloride** (Fig. 2). The constancy of the capacity was satisfactory ; unfortunately, calculated values of sufficient accuracy are not available.

**Sodium Hydroxide** (Fig. 3).    *Natriumhydroxid aus Natrium* was used.    For all values of cathodic polarisation which did not exceed 0·8 V. the capacity showed a marked decrease with time.    For instance at a polarisation of 0·4 V. the capacity of a fresh surface, measured about thirty seconds after its formation was 21·2, after five minutes—19·4 $\mu F/cm.^2$    Renewal of the surface restored the original value.    The same effect was observed after a strong cathodic polarisation (1·5 V.) during a few minutes. The full drawn curve refers to surfaces which were forty-five seconds old, but some points were taken after a cathodic polarisation.    Nevertheless, as shown by Fig. 3, the effect of contamination could not be completely avoided.    In the region of the ascending branch of the electrocapillary curve, the observed values are distinctly lower than the calculated ones.

**Sulphuric Acid** (Fig. 4).    Two specimens were used : one was $H_2SO_4$ *zur Analyse, mit Garantieschein* from Kahlbaum (I), and the other was



Norm. NaOH.    ▣ Observed values, fresh surface.    △ After 5 mins.; × Calculated from electrocapillary curve of ca. 2 norm. KOH.
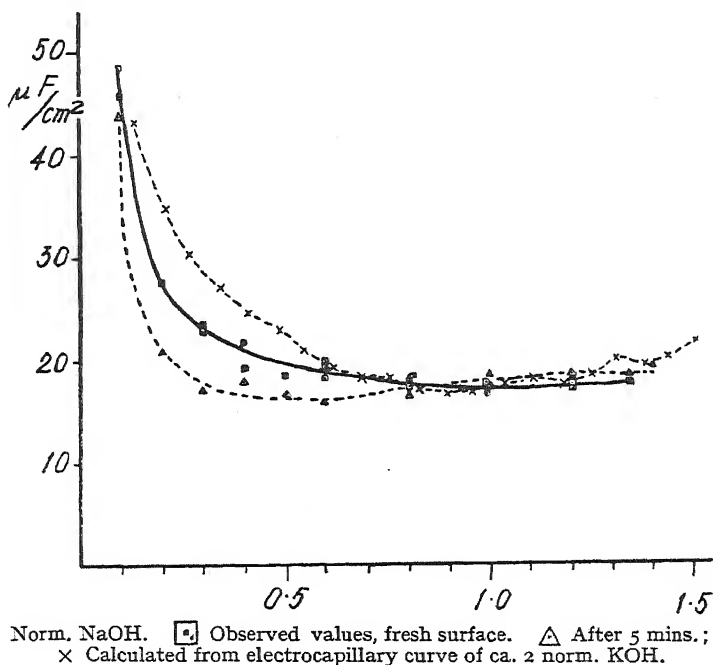
Fig. 3.

obtained by distilling fuming sulphuric acid (II).    The measurements with sulphuric acid were more difficult to carry out than those recorded above, except at the cathodic end of the curve.    At polarisations above 0·6 V. the capacity decreases with time as in the case of NaOH.    At lower polarisations, especially in the neighbourhood of 0·5 V., a fairly rapid rise of the capacity is observed, as if some capillary active anion was adsorbed. The deviations of the experimental curve from the calculated one show, that the influence of the contamination could not be completely avoided even with a fresh surface.    The value of the capacity in the overvoltage region (18-20 $\mu F/cm.^2$) is much higher than the values given by other investigators.    Fig. 4 also shows the influence on the capacity of a contact with paraffin.

**Sodium Sulphate Saturated with Octyl Alcohol** (Fig. 5).    The capacity curve shows two maxima and a strong depression in the middle part.    The anodic and cathodic ends coincide with the sodium sulphate

curve. This is what we ought to expect from the electro-capillary curve,[7] which shows that higher aliphatic alcohols are strongly adsorbed in the neighbourhood of the electrocapillary maximum and that the adsorption disappears rather abruptly in definite narrow intervals of the ascending and descending branch. In these intervals the amount adsorbed changes very strongly with the potential. This causes an increase of the capacity. The position of the capacity maxima is in a fair agreement with the form of the electrocapillary curve. A more detailed theory of these interesting phenomena will be given elsewhere.
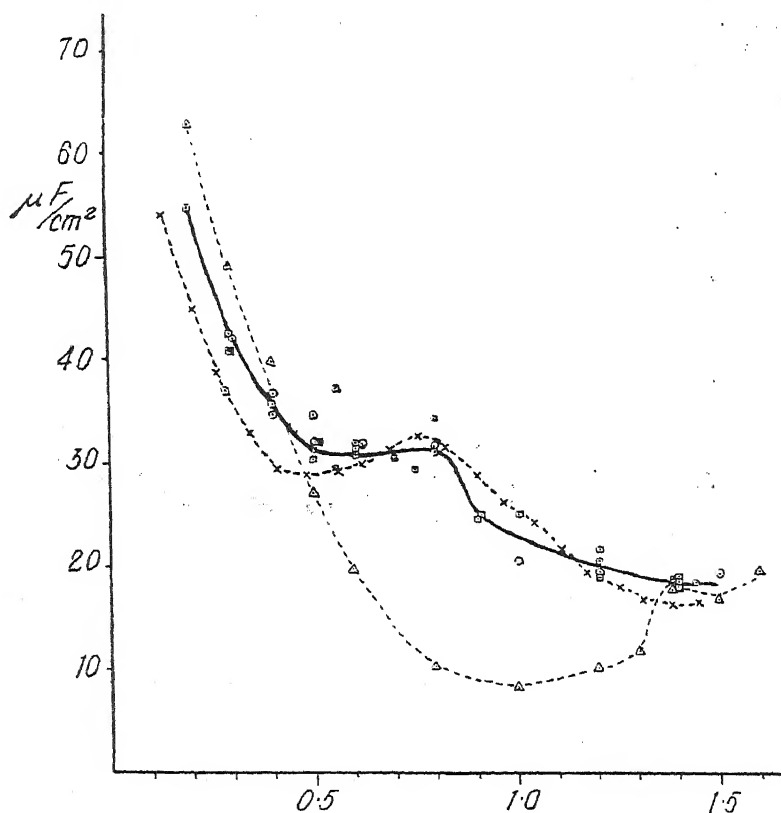


Norm. $H_2SO_4$. ⊡ Observed values with fresh surface, specimen I. ⊙ Same, specimen II. △ After contamination with paraffin. Calculated from electro-capillary curve.

FIG. 4.

The results recorded in this paper show that the observed values of the capacity agree fairly well with the values calculated from electro-capillary data, which can be therefore considered as a sound basis for any further theoretical developments. The remaining discrepancies can be accounted for by traces of contaminations, which we could not avoid.

We cannot give at the present moment a definitive interpretation of the lower values which have been observed by previous authors. It

[7] Gouy, *Ann. physique*, (8), **8**, 291, 1906; Frumkin, *Z. Physik.*, **35**, 792, 1926.

appears however that the danger of contamination has not been realised to a sufficient extent. This applies especially to the apparatus of Erdey
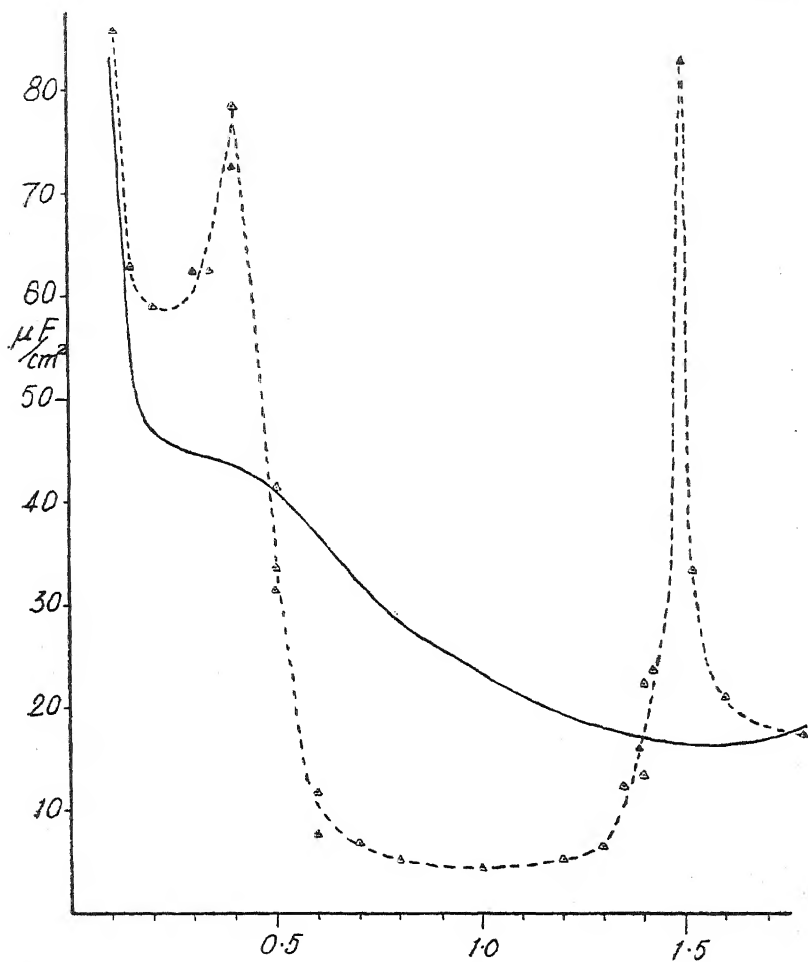


Full line — norm. $Na_2SO_4$.  △ norm. $Na_2SO_4$ saturated with octyl alcohol.

FIG. 5.

Gruz and Kromrey, as they introduced picein in the interior of their cell. The curves given by these authors are very similar to those which we observed with notoriously contaminated surfaces.

*Moscow,*
*Karpow Institute.*

# ON THE CATAPHORESIS OF COLLOIDAL ELECTROLYTES.

By Ian Kemp and Eric K. Rideal.

In a number of disperse colloidal systems the presence of charged particles, the ionic micelles, has been identified by various methods. If the ionic micelle is to be regarded as a large polyvalent ion it should be possible to apply to such systems the modern theory of strong electrolytes. This has been attempted both by Debye and Hückel,[1] by Hückel,[2] and by Henry.[3] In these investigations the colloid particle is regarded as a large polyvalent ion of constant valency surrounded by a diffuse ionic atmosphere of the type postulated by Debye and Hückel.[4] The more detailed analysis of Henry shows that on the above assumptions the relationship between the " ionic " or " cataphoretic " mobility of the spherical particle and the concentration of the electrolyte may be written

$$U = \frac{\chi\sigma}{\eta} \frac{a}{1 + Ka} f(Ka),$$

where $\chi$ is the field strength, $\sigma$ the surface density of charge, $\eta$ the viscosity of the medium, $a$ the radius of the particle, $K = 1/\text{thickness of}$ double layer $= A\sqrt{\mu}$ where $\mu$ is the ionic strength. $f(Ka)$ has been computed as the approximate sum of a series by Henry.[3]

The assumption that the particle is one of constant valency cannot be realised in actual fact since the charge density $\sigma$ depends upon the ionic interchange at the surface of the particle. Such an exchange may be brought about by two processes ; a chemical one, *i.e.*, dissociation of ionisable groups forming part of the surface ; and a process of physical adsorption involving selective or excess adsorption of one ionic species of salts present in the surrounding medium. In the former case the charge will be determined mainly by the activity of the cognate ionic species, whilst for the latter the charge is affected by the addition of any ion which is capable of adsorption. The charge on the particle may be due to both processes and it is possible in some cases to determine the contribution of each, as has been attempted by Price and Lewis.[5] In the case of crystalline quartz the charge is almost entirely defined by selective onic adsorption and with suitable electrolytes it is possible to find ranges of concentration where the excess ionic adsorption is such that $\sigma \sim a\sqrt{\mu}$, *i.e.*, the mobility becomes independent of the ionic strength (Fig. 1).

On the other hand, for micelles of colloidal acids, bases and ampholytes the ionic charge is determined in the main by the $a_{+}^{H}$ of the solution, and variation in the activity of the other ionic species will have little effect since the adsorption of ions is not pronounced. Nevertheless,

[1] *Physik. Z.*, **25**, 44, 1924.    [2] *Ibid.*, **25**, 205, 1924.    [3] *P.R.S.*, **133A**, 156, 1931.
[4] *Physik. Z.*, **24**, 155, 1923.    [5] *Trans. Faraday Soc.*, **29**, 775, 1181, 1923.

even in such systems variations in the apparent micellar valency are to be expected on two accounts :

(1) In strong solutions of electrolytes, especially in the presence of polyvalent or organic ions, ionic adsorption may occur.

(2) In very dilute solutions of electrolytes the effective charge may be modified by the existence of a Donnan ionic equilibrium between cognate ions at the diffuse layer.   In the micelle the dissociating colloidal ions are bound at the surface of the particle and this restriction leads to the establishment of such an ionic equilibrium of the diffusible ions.

The present communication is a brief account of an investigation into the importance of these two factors in limiting the applicability of the theory of Debye and Hückel to the mobility of protein systems.
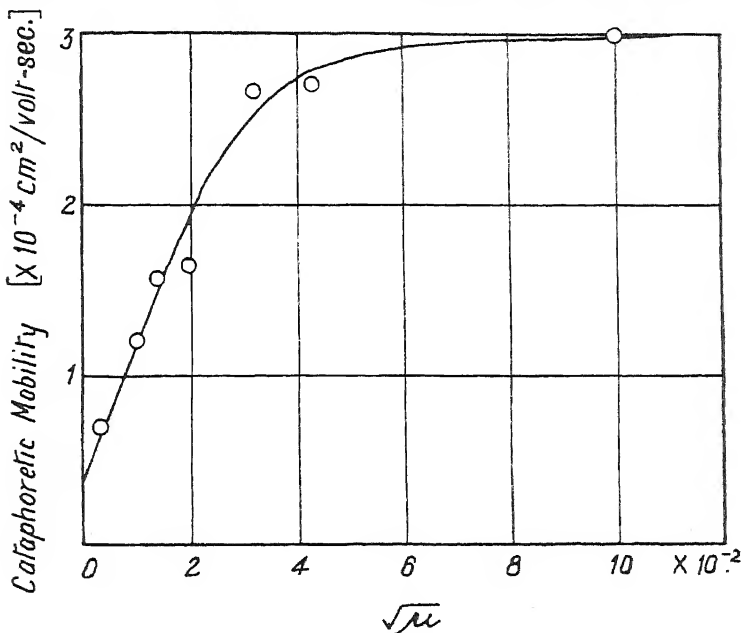


FIG. 1.—Relation between mobility of quartz and ionic strength of KCl.

## Experimental.

The systems investigated were

    (a) sols of gliadin

    (b) suspensions of quartz particles covered with adsorbed gliadin.

The mean radius of the particles was determined by two independent methods :—

(1) Measurement of the Brownian displacements as a function of the time.

(2) For the quartz particles the first method was checked by the usual process of counting evaporation and weighing.

Both methods gave consistent results in agreement with one another yielding a mean radius of $a = 0.125\mu$ ($\pm 0.010\mu$).

The surface density of charge $\sigma$ was determined by electrometric titration of the gliadin suspension employing the quinhydrone electrode.

Since the protein concentration never exceeded 0·5 per cent., no sensible protein error was introduced, but a correction was made for the secondary salt effect following the method suggested by Linderstrom, Lang and Lund.[6] The values found for the dissociation constants of gliadin were

$$pKa = 5 \cdot 9 \quad \text{and} \quad pKb = 9 \cdot 8.$$

The mass of gliadin occupying unit area of the quartz surface was computed from the data on the spreading of monolayers of gliadin given by Hughes and Rideal.[7]

For the determination of the cataphoretic velocity U a micro-cataphoresis apparatus of the Mattson type [8] in conjunction with a Leitz slit ultramicroscope was employed.

The hydrogen ion activities of the solution were measured by means of the hydrogen and whenever possible by means of the quinhydrone electrode as well. From the cataphoretic mobilities of the particles in sodium acetate acetic acid buffer solutions as a function of the hydrogen
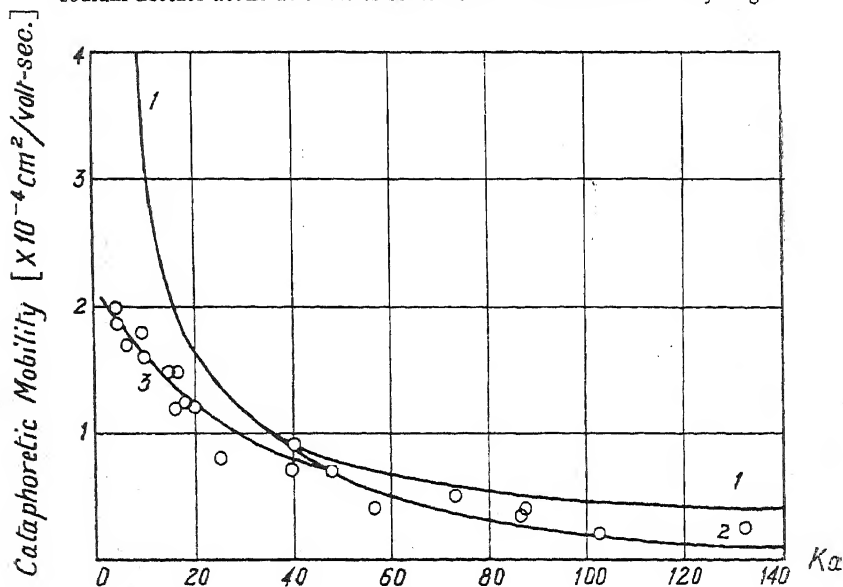


FIG. 2.

ion activity, the acid and basic dissociation constants could also be obtained although a somewhat extended extrapolation was required. The values obtained were $pKa = 5 \cdot 5$ and $pKb = 9 \cdot 7$. It is interesting to note that the isoelectric point derived from these figures is not in agreement with the accepted value for gliadin, viz. $Pa_H = 6 \cdot 5$ determined from turbidity and solubility measurements. This value of $Pa_H = 6 \cdot 5$ for the point of minimum solubility we have confirmed.

For the examination of the mobility as a function of the ionic strength a standard $Pa_H = 4 \cdot 40$ was adopted, the particles being positively charged under these conditions.

In Fig. 2 is given the theoretical curve (1·1) calculated according to the method of Debye-Hückel and of Henry which is compared with the experimentally determined mobilities. It is interesting to note that a surprisingly good agreement (in view of the possible errors in the evaluation of the two unknown factors, the surface charge $\sigma$ and the particle

[6] C.R. Trav. Lab. Carlsberg, 16, 5, 1926.    [7] P.R.S., 137A, 162, 1932.
[8] J. Physic. Chem., 32, 1532, 1928 ; 37, 223, 1933.

radius $a$), is obtained, but only between values of $Ka$ from 35 to 45, that is for a range of ionic strength from $\mu = 0 \cdot 008$ to $\mu = 0 \cdot 013$. Both below and above this region the observed mobilities are considerably less than those computed by the simple theory.

## Discussion.

The discrepancy between the observed and calculated mobilities at high ionic strengths may be ascribed as we have suggested to the occurrence of an appreciable adsorption of ions from the electrolyte ; in this case the acetate ions are preferentially adsorbed, thus giving a reduced mobility due to a decrease in $\sigma$ at high ionic strengths. The adsorption of acetate ions in these concentrations of electrolytes can be confirmed and measured from the effect of the electrolyte concentration on the iso-electric point of gliadin. From the shift in the iso-electric points the acetate ion adsorption has been determined and found to yield a Langmuir adsorption isotherm. From the values was obtained a corrected surface density of charge and hence a corrected mobility assuming the continued validity of the Debye-Hückel and Henry expression. The corrected curve is given in Fig. 2 ($1 \cdot 2$) and as will be seen is in reasonable agreement with the observed mobilities.

In order to account for the divergence in solutions more dilute than $\mu = 0 \cdot 008$ we must consider that in very dilute solutions the electrolyte within and outside the effective double layer will not be of identical composition, for the gliadin ions may be regarded as being under restraint by attachment to the relatively imponderable molecules attached to or forming part of the micelle ; this gives us the necessary conditions for the establishment of an ionic equilibrium governed by Donnan's distribution law. If we designate by the suffix 2 the ionic activity within the double layer and by 1 those outside, it can be shown that the charge on the gliadin ion inside is given by

$$n_2 = n_1 \sqrt{\dfrac{CH_3COO^1}{\overset{+}{G}n_1 + CH_3COO^1}},$$

where $G$ = activity of gliadin,
$(CH_3COO^1)$ = activity of acetate,
$n_1$ = charge at $Pa_H$ of the outer liquid.

Thus in strong solutions $n_2 = n_1$ or the gliadin ion possesses a charge which is the same as that associated with the hydrogen ion concentration of the external fluid but as the concentration of the external electrolyte decreases the effective valency decreases. From the experimental curve it is seen that $n_2 = n_1$ at a concentration of electrolytes corresponding to $Ka = $ ca . 45, $\mu = 0 \cdot 008$. It is possible to calculate the effective concentration of gliadin ions within the double layer. Assuming the validity of the applicability of the Donnan distribution law the alteration in the charge of the gliadin ions with the variation in electrolyte concentration has been calculated and hence the modified surface charge densities $\sigma$. From these values of $\sigma$ the mobilities have been calculated with the aid of the Debye-Hückel-Henry expression and it is seen that the resulting curve ($3 \cdot 2$) is in good agreement with the experimentally determined values.

Preliminary experiments on the actual Donnan membrane potential have shown that with gliadin solutions of this concentration the membrane potential actually falls to extremely small values in acetate solutions when the concentration is raised to $\mu = 0 \cdot 008$.

## Summary.

The Debye-Henry expression for the cataphoretic velocity is, for the systems investigated, applicable only over a limited range of electrolyte concentration.

For stronger solutions, appreciable adsorption of anions leads to discrepancies. For very dilute solutions, the effective valency of the ion is reduced owing to the existence of a Donnan ionic equilibrium at the ionic envelope.

The suggestion is supported by preliminary experimental evidence.

# THE SIGNIFICANCE AND DETERMINATION OF MOBILITIES IN THE STUDY OF COLLOIDAL ELECTROLYTES.

By John L. Moilliet, B. Collie, Conmar Robinson and
G. S. Hartley.

It was pointed out by McBain [1] that the equivalent conductivity of an electrolyte would be increased by the aggregation of ions of one kind to form ionic micelles, and such aggregation was therefore put forward by him as the explanation of the remarkable increase of equivalent conductivity with increasing concentration observed [2] in the aqueous solutions of soaps at about $N/10$ and higher concentrations. This prediction is a direct outcome of Stokes' law if assumed applicable to the movement of ions in the electric field. If we are dealing with spherical ions of radius $r$ and $m$ such ions aggregate to form micelles, also spherical, the radius of the micelles, assuming the closest possible packing of the constituent ions, will be $r \cdot m^{\frac{1}{3}}$. Now the resistance to motion offered by spherical particles is, according to Stokes' law, proportional to their radius, and the total resistance to motion of the $m$ ions will therefore be, after aggregation to one micelle, a fraction $(r.m^{\frac{1}{3}})/(r.m) = m^{-\frac{2}{3}}$ of its former value. The force acting on them due to the external field will be unaltered and therefore their velocity will be multiplied by $m^{\frac{2}{3}}$, and, as they carry the same amount of electricity as before, their contribution to the conductivity will be multiplied by the same amount.

In addition to the assumptions of spherical particles and close packing, we have so far assumed that we are dealing with a solution so dilute that association of oppositely charged ions (*i.e.*, inclusion of " gegenions " in the micelle,[3] referred to subsequently as the " inclusion " effect) and the depression of mobilities due to the effect of the Coulomb forces between the free ions, as considered in the Debye-Hückel-Onsager theory (the latter will be referred to as the " atmosphere " effect) are both

[1] McBain, *Trans. Faraday Soc.*, **9**, 99, 1913.

[2] See *i.a.* McBain and Taylor, *Z. physikal. Chem.*, **76**, 179, 1911 ; Bunbury and Martin, *J. Chem. Soc.*, **105**, 417, 1917 ; McBain, Laing and Titley, *J. Chem. Soc.*, **115**, 1279, 1919.

[3] By " micelle " we mean the central multivalent complex bound together, at least momentarily, as a single kinetic unit—the *mizellion* of Wintgen. We use the word *gegenions*, for want of a better, to denote the simple oppositely charged ions whether bound in the micelle or not. The micelle is thus regarded as an aggregate of ions of one kind plus a certain number of gegenions adhering to them.

negligible.   In practice this assumption cannot be made, for even in the most dilute micelle-containing solutions that can be examined, the necessary presence of multivalent ions (the micelles), with a valence of the order of 10 or 20, will cause both of these effects to be abnormally large as compared with those in ordinary electrolytes.   These secondary effects (as distinguished from the " primary " or " Stokes' law " effect of aggregation) will be of course greater the greater the number of ions aggregating to one micelle, and thus the factors tending to lower the conductivity will increase with that tending to increase it, so that it is to be expected that the increase of conductivity on aggregation will be at least considerably levelled out.   This means that it may be impossible
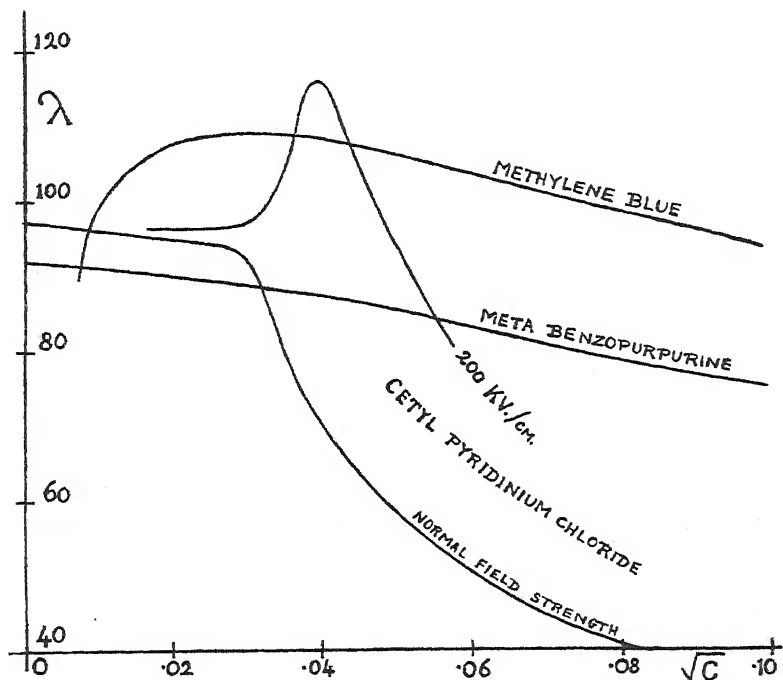


FIG. 1.

to obtain from conductivity measurements alone direct evidence of the formation of ionic micelles.

This difficulty will be seen by reference to the conductivity concentration curves shown in Fig. 1, for substances in all of which aggregation (evidence for which will be given later) occurs.   Methylene Blue [4] ions aggregate in very dilute solution where the secondary effects are small, and consequently a rise of equivalent conductivity with increasing concentration is obtained, which gives place at about $N/1000$ to a fall as the secondary effects predominate.   In the case of *meta* Benzopurpurine,[5] the primary and secondary effects balance one another and no considerable departure from the normal is apparent.   Cetyl pyridinium chloride shows

[4] See the paper by Robinson (p. 245) read at this meeting.
[5] See references (4) and (12).

no aggregation below a concentration of nearly $N/1000$, and in this case the secondary effects are here so great that a sharp *fall* of conductivity [6] results.   Rather striking evidence that the fall *is* due to the secondary effects, both of which would be diminished if the atmospheres of the micelles could be removed, has recently been obtained by measurements of the conductivity in very strong fields [7] which partially accomplish this removal.[8]   The equivalent conductivity of this substance in a field of 200 KV./cm. is also shown on the figure, and it will be seen that a sharp *rise* above the infinite dilution value occurs at the same concentration where the normal conductivity shows the fall.

At much higher concentrations $(N/10$ and above) the long-chain salts in general, of which cetyl pyridinium chloride is a typical example, show a slow rise of conductivity with increasing concentration.   It was this behaviour in the case of the soaps which, as mentioned above, first led McBain to put forward the hypothesis of the ionic micelle. Lottermoser [9] accepts this explanation of the similar behaviour of the salts of the higher alkylsulphuric acids.   In view, however, of the fact that the secondary effects already outweigh the primary effect at so low a concentration as $N/1000$, we hesitate to believe that at much higher concentrations the reverse will be true of further aggregation, unless, for some at present little understood reason,[10] the secondary effects actually decrease with increasing concentration in these concentrated solutions, in which case it would be unnecessary to assume that further aggregation occurs.   In the present state of our theoretical knowledge we feel that it is premature to draw any definite conclusions from the behaviour of these substances in concentrated solution.

Since the equivalent conductivity as a function of concentration may give little or no evidence of aggregation, it is of great importance to obtain accurate data for quantities which almost certainly will.   Such quantities are the transport numbers and mobilities.   The primary effect of aggregation is to increase the mobility $V_R$ of the aggregating radical which we will denote by **R** while leaving the mobility $U_A$ of the simple radical **A** unchanged.   The transport number $T_R$ of the aggregating radical will be increased.   The atmosphere effect will decrease both $U_A$ and $V_R$, but $V_R$ more than $U_A$, since the effect on multivalent is greater than on univalent,[11] and hence it will decrease $T_R$.   It is unlikely, however, that this effect alone will be greater than the primary effect, and we should therefore expect the resultant effect to be an increase of both $V_R$ and $T_R$. The effect of the inclusion of **A** ions in the micelle on $V_R$ and $T_R$ may best be made clear by consideration of the quantitative relationships in the simplified case where all the **R** ions are assumed to exist in the form of micelles of one kind and where a fraction $(1 - f)$ of the **A** ions is included in these micelles and equally distributed amongst them. The observed mobility $V_R$ of the **R** radicals will in this case be equal to the mobility of the micelles, which will be, in the absence of atmospheric

[6] Unpublished measurements by Hartley.

[7] Measurements of Malsch and Hartley, to be published in *Z. physikal. Chem.*

[8] See the theory by Joos and Blumentritt (*Physikal. Z.*, **29**, 755, 1928) of the well-known results of Wien (*i.a. ibid.*, p. 751).

[9] *Koll. Z.*, **63**, 175, 1933.

[10] See the discussion by Hartley in another paper (No. 6) to be read at this meeting.

[11] As will be apparent from an examination of the equation of Onsager (*Physikal. Z.*, **28**, 277, 1927) for the mobilities of ions in a dilute solution of a pure electrolyte.   See also paper by Hartley, ref. (10).

effects, proportional to their charge and hence to $f$, so that we may, when considering the effect of inclusion alone, write

$$V_R = K \cdot f. \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

Now the free **A** ions will have a mobility which we will denote $L_A$ and the bound ones will necessarily have a mobility $= -V_R$. Their observed mobility $U_A$ may therefore be written

$$U_A = f \cdot L_A - (1 - f) \cdot V_R, \qquad . \qquad . \qquad . \qquad (2)$$

which, for consideration of the effect of inclusion alone, we may write, by substitution from (1),

$$\begin{aligned} U_A &= f \cdot L_A - (1 - f) \cdot f \cdot K \\ &= f \cdot (L_A - (1 - f) \cdot K). \qquad . \qquad . \qquad . \qquad (3) \end{aligned}$$

The factor inside the bracket in equation (3) will decrease as $f$ decreases, i.e., as the inclusion increases, and therefore $U_A$ will decrease with increasing inclusion relatively more rapidly than $f$ and therefore than $V_R$. The transport number $T_R$ will therefore be increased by the inclusion process, while the mobility $V_R$ will be decreased. It will be useful perhaps to summarise these conclusions in tabular form :—

| Cause. | Effect on | | | |
|---|---|---|---|---|
| | $U_A$. | $V_R$. | $\Lambda = U_A + V_R$. | $T_R = V_R/\Lambda$. |
| Aggregation | nil | large increase | large increase | increase |
| Ionic atmospheres | small decrease | decrease larger than that of $U_A$ | decrease | decrease |
| Inclusion of A ions in micelle | large decrease | decrease much smaller than that of $U_A$ | large decrease | large increase |

It will be seen from this table that we are likely to find an increase of mobility of the aggregating radical even when the secondary effects are too great to permit the equivalent conductivity of the whole electrolyte to show an increase. Further, the transport number of the aggregating radical may be expected to continue to increase still higher up the concentration scale than the mobility, and for this reason the transport number might be considered the quantity most sensitive to aggregation. An increasing mobility is, however, if obtained, more satisfactory evidence of aggregation in that while the mobility is increasing the aggregation must also be increasing. It is probable that the secondary effects will cause the mobility to decrease again before the aggregation has ceased to increase, and that the transport number would still be found to be increasing, but this latter fact is in itself evidence only that aggregation has occurred and not that it is still occurring.

The results of measurements by Moilliet of the mobilities of the electronegative radical of some benzidine dyes, using the moving boundary method, are given in Fig. 2 of the paper contributed by Robinson to this meeting (No. **23**), where they are further discussed. It may be said here that *meta* Benzopurpurine, whose apparently normal conductivity curve has already been remarked on, shows a mobility increasing with increasing concentration in dilute solution, giving definite evidence of aggregation.

Bordeaux Extra shows the same phenomenon in lesser degree.   The
mobility of Benzopurpurine 4B is decreasing with increasing concentra-
tion throughout the whole range investigated, but as its infinite dilution
value will probably not be very different from that of the " meta " dye,
a rising mobility would probably have been found at still lower con-
centrations if it had been possible to carry out the measurements there.

   The transport numbers of the electronegative radical in these dyes
are shown in Fig. 2 of this paper.   All show a considerable rise with
increasing concentration giving evidence of the presence of anionic
aggregates of high valence which include more of the simple cation as
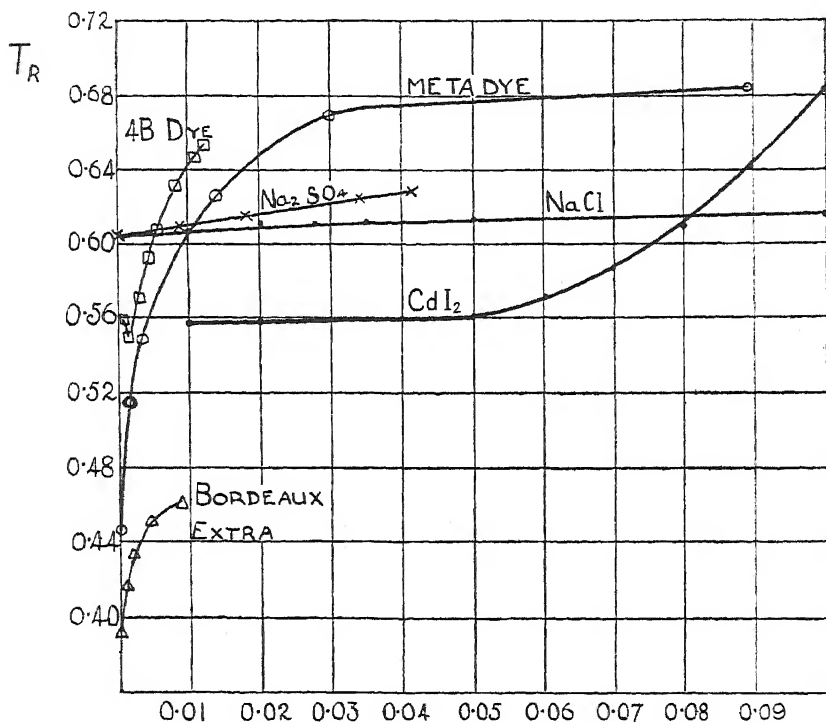


FIG. 2.

the concentration is increased.   For comparison are shown also the
values for two ordinary electrolytes and for cadmium iodide, in which,
as is well-known, complex ions of the type $(CdI_4)^=$ are formed.   For
further details, the paper of Robinson and Moilliet [12] should be consulted.

   We have no mobility data available for cetyl pyridinium chloride.
Collie has, however, made some measurements on the bromide, which
we have no reason to believe is markedly different in properties, by the
Balanced Boundary method, which will be referred to again later.
Unfortunately he has as yet data at only two concentrations and these
have not therefore been shown on the figure.   The values determined

[12] Robinson and Moilliet, *Proc. Roy. Soc.*, 143 A, 630, 1934.

at 35° C. are 50·5 at 0·035 $N$ and 30·8 at 0·11 $N$ (in this case for the electro-positive radical). The value at infinite dilution (obtained from the conductivity curve for the chloride at 25° C. and corrected for the temperature difference) will be approximately 26. It will be seen that in this case we have a very large increase between zero concentration and $N/30$, the greater part of which will presumably occur in the region where the equivalent conductivity is rapidly falling. The transport numbers at these two concentrations are 1·71 and 1·08 respectively, and the infinite dilution value will be about 0·23. A similar variation of transport number with concentration is found in the soaps with which measurements have been made by the Hittorf method,[13] but no solutions of concentration lower than 0·25 $N$ have been, as far as we are aware, examined, except in the case of potassium laurate where $T_-$ at 0·05 $N$ is 0·28, indicating that aggregation has not at that concentration commenced. At higher concentrations of this salt and of potassium and sodium oleates the transport number falls with increasing concentration. Values of $T_-$ greater than 1 have not been found for the potassium salts, but for sodium oleate (Laing) it ranges from 1·22 at 0·2 $N$ to 1·05 at 0·6 $N$ : in soap curds it is much higher.

From the mobilities, we may also obtain on certain assumptions some indication of the amount of the gegenions included in the micelles. The fraction of them included is the quantity $(1 - f)$ of equation (2). Multiplying this equation through by the Faraday to convert the mobilities to the equivalent conductivities, denoted by the corresponding small letters, and adding $v_R$ to both sides, we obtain

$$\lambda = f \cdot (l_A + v_B). \qquad . \qquad . \qquad . \quad (4)$$

Since $\lambda$ and $v_R$ are measurable quantities, we may obtain $f$ from this equation if we can make some reasonable assumption as to the value of $l_A$. In deriving equation (4) the assumption was made that only one micellar type existed. Actually several at least slightly different types will exist in rapid equilibrium. The limited significance of the values of $f$ obtained should therefore be recognised. In cases where this assumption of a unique micelle could reasonably be made, it would be further possible, if the atmosphere effect could be corrected for so as to obtain the "Stokes' law mobility," to calculate the number of ions in the micelle.

Robinson and Moilliet [12] calculated values for $f$ in the case of the dyes mentioned above, taking $l_{Na}$ to be equal to $u_{Na}$ in equinormal solutions of NaCl or $Na_2SO_4$. The values obtained on these two alternative assumptions were not very different, and it could be concluded that only a small fraction of the sodium was contained in the Bordeaux Extra micelles, but that those of the benzopurpurines contained appreciably more.

A similar calculation from Collie's results for cetyl pyridinium bromide shows that either a value of $l_{Br}$ must be taken that is higher than the infinite dilution value (!) or it must be concluded that the fraction $f$ of free bromide ions is higher in $N/10$ solution than in $N/30$. The significance of this conclusion must of course await further research. The values of $f$, taking the infinite dilution value of $l_{Br}$, are about 0·22 at $N/30$ and 0·24 at $N/10$. We are presumably dealing here with very much larger micelles than in the dyes, and these, in consequence of their

[13] McBain and Bowden, *J. Chem. Soc.*, **123**, 2417, 1923 ; Laing, *J. Physic. Chem.*, **28**, 673, 1924 ; Holroyd and Rhodes, *J. Chem. Soc.*, **125**, 438, 1924.

much higher primary charge, include a very much larger fraction of the gegenions (at least 75 per cent. in these concentrations).

It is interesting to note that we may obtain valuable confirmation of the purity of the colloidal electrolytes under investigation from the plot of the mobility of the simple radical against concentration. Thus Robinson and Moilliet [12] found that the $u_{Na}$ values for *meta* benzopurpurine and Bordeaux Extra extrapolated satisfactorily to 50·1, the value of $u_{Na}$ at infinite dilution obtained by MacInnes, Longsworth and Shedlovsky.[14] Any appreciable contamination in the solutions of the dyes would have given high values for $\lambda$ and hence high values for $u_{Na}$. The values for the 4B dye could not be extrapolated, as the form of the curve in very dilute solution was obviously in doubt, but the values actually obtained in the most dilute solutions were considerably lower than 50·1, a fact which could not possibly be explained by impurity.

## The Moving Boundary Method.

The most accurate method for the determination of transport numbers is the moving boundary method as developed by MacInnes and his collaborators for ordinary electrolytes. A general review of the method has been given by MacInnes and Longsworth.[15] The theory has been treated from a somewhat different angle by Hartley and Moilliet.[16] It has been shown that if a solution **AR** lies below one of **AX, A** being the common, for example electropositive, radical, a *sharp* boundary will move downward when negative current flows downward, provided that the following conditions are satisfied : (*a*) The **AR** solution must be heavier than the **AX** solution. (*b*) The disturbing effects of convection, electrolysis products, hydrolysis and endosmosis must be absent. (*c*) The **R** radical must be more mobile than the radical **X**, both in their respective solutions *and in any mixture of the two that may arise at the boundary*. The last clause needs special emphasis when we are dealing with colloidal electrolytes, as it then ceases to be mere pedantry and becomes of practical importance. A solution so dilute in leading radical that the latter exists in its simple ionic form must occur just above the boundary and it is therefore necessary for the indicator to be slower than the *simple* as well as the aggregated ions. This is practically achievable with divalent dyes, but it is probably impossible with univalent long-chain salts and dyes. For such substances (*i.e.*, of very low radical mobility) the Balanced Boundary method, which we will discuss in the next section, was devised.

**R** is called the leading radical, **AR** the leading electrolyte, and **AX** and **X** are called indicator and indicator radical respectively. As has been previously shown [16] the concentration $c_R$ of the leading electrolyte **AR** remains constant on the passage of the current, while the new indicator solution formed below the original position of the boundary must satisfy the equation of Kohlrausch

$$\frac{T_R}{c_R} = \frac{T_X^K}{c_X^K}, \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (5)$$

where $T_R$ is the transport number of the leading radical and $T_X$ that of the indicator radical and where the index $K$ refers to the new indicator solution. The sharpness of the boundary is maintained by the fact

[14] MacInnes, Longsworth and Shedlovsky, *J. Am. Chem. Soc.*, **54**, 2758, 1934.
[15] MacInnes and Longsworth, *Chem. Reviews*, **11**, 171, 1932.
[16] Hartley and Moilliet, *Proc. Roy. Soc.*, **140A**, 141, 1933.

that any leading radical lagging behind the boundary will find itself in a region of higher potential gradient than before and will be accelerated,[17] and any indicator radical diffusing below the boundary will find itself in a region of lower potential gradient and will lag behind. If $c_R$ be the concentration of the leading electrolyte in gm.-equivalents per c.c. and if the boundary advances through $V$ c.c. in $t$ secs., while a current of $I$ amps. is flowing, then

$$T_R = \frac{V \cdot F \cdot c_R}{I \cdot t}, \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \quad (6)$$

where $F$ is the Faraday in coulombs per gm.-equivalent. While an experiment is proceeding the current is kept constant by means of a variable resistance in the electrical circuit. The velocity of the boundary then remains constant if the conditions laid down above are fulfilled, and the constancy of the velocity is therefore a very useful test of their fulfilment.

This method gave satisfactory results with " meta " benzopurpurine, benzopurpurine 4B and Bordeaux Extra. For the first two dyes, sodium benzoate was used as indicator. For Bordeaux Extra, however, the radical mobility was considerably lower and consequently a slower indicator radical was required and $\alpha$-napthalene sulphonate was found to be suitable. The results obtained were reproducible to one part in 500.

## The Balanced Boundary Method.

This method was devised for the measurements of the transport numbers of those colloidal electrolytes (such as cetyl pyridinium bromide) the mobilities of whose aggregating radicals are so low that it is impossible to find an indicator whose radical of like polarity has a sufficiently low mobility, in which case, as has already been stated, the ordinary moving boundary method is no longer applicable. It has been worked out by Hartley, Drew and Collie [18] in the case of ordinary electrolytes, and enables the sharpening principle of the moving boundary, which, as these authors show, is responsible for the greater accuracy of this method as compared with the Hittorf method, to be made use of for these substances, the radical whose mobility it is desired to measure being placed in the " indicator " position. Since the concentration of " indicator " in the new " Kohlrausch " solution formed in the region evacuated by the boundary will be different from the initial concentration, it must be measured. Actually a leading radical whose transport number is known is used and the unknown transport number of the following radical is obtained from the measured Kohlrausch concentration and the concentration and transport number of the leading electrolyte by means of equation (5).

[17] The Kohlrausch equation can be written in the form

$$\frac{v_R}{\kappa_R} = \frac{v_X^K}{\kappa_X^K},$$

from which it follows that, as $v_R$ is greater than $v_X$, the specific conductivity $\kappa_X^K$ of the Kohlrausch solution is less than that of $\kappa_R$ of the leading solution, and hence the potential gradient in the former is greater than that in the latter, the potential gradients being in fact in such a ratio that the actual velocities of the leading and indicator radicals in their respective solutions are equal.

[18] Hartley, Drew and Collie, *Trans. Faraday Soc.*, **30**, 648, 1934.

The balanced boundary method was designed to enable this concentration to be measured, and this is done by continuous slow displacement of the Kohlrausch solution as it is formed into a side tube fitted with electrodes for conductivity determination. It was found necessary to displace the solution very slowly in order to avoid convection trouble, and it therefore had to be done continuously while the current was flowing, in order that the boundary should be maintained sharp and trouble due to diffusion also avoided. Displacement of a sufficiently slow and easily regulated velocity was obtained by means of a glass piston whose rate of fall was controlled by a clock.

## The Moving Boundary Method in Mixtures and Colloids.

The moving boundary method may be applied to the measurement of mobilities in mixed electrolytes,[19] provided that the mobility of the radical to be investigated is greater than that of any others of like polarity present. In this case the boundary will be sharp, but the less sharp the greater the proportion of other electrolytes present. The Kohlrausch solution will here be formed largely of the slower ions left behind as the boundary advances, and will consist entirely of these if the only radicals contained in the initial supernatant liquid which are of like polarity with the leading one are slower than all of those contained in the solution below the original boundary : in the latter case a second boundary with which we shall not be primarily concerned will be formed. It is only necessary that the indicator solution should contain no radicals of like polarity with the leading radical which are faster than the leading radical. If this condition is not fulfilled or if the original solution below the boundary contains radicals which are faster than the one whose mobility is to be measured, the composition of the solution below the boundary of the latter (which will have no tendency to sharpen) cannot remain unchanged. Measurements in such a system are useless.

The conditions under which the cataphoresis of colloids can be measured by the moving boundary method has been the subject of considerable confusion in the past.[20] The consideration of the theoretical principles we have just discussed in the case of colloidal electrolytes are particularly helpful in allowing us to see this problem in its essentials. The following remarks on the general problem will not therefore be out of place here. An aqueous sol consists essentially of charged particles necessarily accompanied by oppositely charged ions and generally containing also a certain amount of other non-colloidal electrolytes, the nature and quantity of which will depend on the method of preparation. From the moving boundary point of view, the sol might be regarded as a mixed electrolyte and we might obtain satisfactory measurements in certain cases if the foregoing conditions are satisfied, and the potential gradient obtained from conductivity and current, and not, as is frequently done, from the total potential drop. It should, however, be mentioned that, as there will here be no equilibrium among the particles, it will be further necessary that they should all have the same velocity.

If the sol, as is probably the case, contains ions more mobile than the

[19] See Longsworth, *J. Am. Chem. Soc.*, **52**, 1897 (1930).
Measurements were successfully carried out by Moilliet on dye solutions to which sodium benzoate had been added, but these have not yet been published.
[20] See however the excellent discussion by Henry and Brittain, *Trans. Faraday Soc.*, **29**, 798, 1933.

particles, the method as ordinarily used [21] cannot be applied, since the composition of the sol is bound to change.    It is probable that this is the cause of most of the unsatisfactory results obtained with ordinary colloids.    In the case of sols such as arsenious sulphide, where the conductivity of the particles is a large fraction of the whole, as has been shown by Kruyt,[22] the ultrafiltrate will not be a suitable supernatant liquid if only because it will contain hydroxyl ions formed by membrane hydrolysis.[23]    Even if it is sometimes possible to find a suitable indicator, nevertheless if the fall of $\zeta$-potential with successive addition of electrolyte is being followed, it seems probable that a point will be reached where, owing to the decrease of the velocity of the particles, the original indicator solution will no longer be suitable and it may be impossible to find a suitable one.    The fact that the interpretation of the electrokinetic properties of sulphide sols has been thought to be different from that of other lyophobic sols may therefore be due to misinterpretation of the cataphoretic measurements.

When we have ions present more mobile than the colloidal particles and of the same sign, satisfactory results *can* be obtained if sufficient electrolyte is present throughout the whole system to make certain that changes of composition produced as the boundary advances will have a negligible effect on the conductivity and hence on the uniformity of the potential gradient.    This condition will probably be satisfied by some sols (*e.g.*, gold sols) without actual addition of electrolyte if the ultrafiltrate is used as supernatant liquid, as electrolyte in this sense sufficient will be present as a result of the method of preparation.    In the study of proteins, where the $p_H$ has to be controlled by buffer solutions, Tiselius [24] made use of this principle.    The boundaries in this case will be diffuse by contrast to the sharpened boundary in the pure electrolyte case, but they may, by virtue of the low diffusion velocity of the particles, remain sufficiently sharp, if sharp when formed, to permit measurements to be made: the mobility of the particles may be obtained from the velocity of either boundary.    Only in this case, when electrolyte is present in sufficient quantity throughout the whole system, will it be possible for the velocity of a boundary to be used as a measure of the mobility of the ions or particles which follow it, unless, as in the Balanced Boundary method or as in the experiments of Hacker,[21] the conductivity of the following solution is determined.

*The Sir William Ramsay Laboratories of*
*Inorganic and Physical Chemistry,*
*University College, London,*
*and Imperial Chemical Industries Limited.*

[21] Hacker (*Koll. Z.*, **62**, 37, 1933) has, however, made successful measurements in which the colloid particles followed the boundary : the " Kohlrausch concentration " of the sol was approximately calculated and then various concentrations near this were tried until the potential gradient in the sol, as determined by " Mukherjee side tubes " remained constant as the boundary advanced.

[22] Kruyt and van der Willigen, *Koll. Z.*, **44**, 22, 1928.

[23] Ingraham, Lombard and Visscher, *J. Gen. Physiol.*, **16**, 637, 1933 ; McBain and McClatchie, *J. Am. Chem. Soc.*, **55**, 1315, 1933 ; see also Robinson and Moilliet, *ref.* (12).

[24] Tiselius, *Nova Acta Upsal.*, (4), **7**, No. 4, 1930.

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# PART I. (B) METHODS AND EXPERIMENTAL TECHNIQUE.

## THE DETERMINATION OF THE ELECTRIC CHARGE OF COLLOIDAL IONS.

### By G. S. Adair and M. E. Adair.

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*Received* 17th *July*, 1934.

Pauli[1] and his colleagues have described methods adapted for the investigation of the valence of colloidal ions in aqueous solutions, or in solutions containing traces of free acids or bases formed by hydrolysis. In systems of this type, the total acid or base equivalent to the colloid is estimated from chemical analyses, supplemented by measurements of the hydrogen ion concentration, and approximate estimates of the valence or " free charge " are obtained by measurements of conductivities, osmotic pressures by direct or indirect methods, and by electrometric measurements of ion activities. The apparent ionisation calculated from such measurements may be lower than the true value, on account of the interionic forces described by Debye and Hückel.[2]

The methods used for the study of the valence of colloidal ions in aqueous solutions are not well adapted for experiments on mixtures of colloidal and crystalloid electrolytes, because it is difficult to allow for the effects of the crystalloids on conductivities and on the total osmotic pressures. Special methods available for such mixtures include the measurement of cataphoresis, of osmotic pressures with membranes permeable by salts, and of membrane potentials.

### Cataphoresis.

Tiselius[3] devised a method for obtaining accurate measurements of the velocity of cataphoresis and showed that it is possible to calculate an apparent valence from such measurements ; he pointed out that the results obtained may be much lower than the real values on account of the interionic forces. This difficulty is discussed by Henry,[4] who has reviewed recent work on the theory and technique of cataphoresis. Abramson[5] has published a formula for the calculation of valence from cataphoresis measurements, but his derivation is not rigorous, as shown by experiments recorded below.

### Osmotic Pressure.

A critical study of the direct method for the measurement of osmotic pressures of colloidal electrolytes such as the proteins, with membranes

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[1] Pauli and Valkó, *Electrochemie der Kolloide*, Wien, 1929 ; *Kolloidchemie der Eiweisskörper*, Dresden und Leipzig, 1933.
  These publications give extensive references to the work of other investigators.
[2] Debye and Hückel, *Physik. Z.*, **24,** 185, 1923.
[3] Tiselius, *Nova Acta Reg. Soc. Sci. Upsaliensis*, Ser. IV, 7, No. 4, 1930, see also Pedersen, *Kolloid Z.*, **63,** 268, 1933.
[4] Henry, *Roy. Soc. Proc. A.*, **133,** 106, 1931.
[5] Abramson, *J. Gen. Physiol.*, **15,** 575, 1932.

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[4] Henry, *Roy. Soc. Proc. A.*, **133,** 106, 1931.
[5] Abramson, *J. Gen. Physiol.*, **15,** 575, 1932.

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permeable by crystalloids, has been published in a previous paper.[6] The observed pressure $p$ can be regarded as the sum of two partial pressures, $p_p$ due to the colloidal ions and $p_i$ attributable to the excess of diffusible ions inside the membrane. Measurements are made with a wide range of concentrations of protein, hydrogen ions and salts, and if evidence is found for the existence of a range of concentrations which satisfies the conditions that $p_i$ must form a large fraction of the total pressure in a solution where the deviations from the ideal solution laws are small, an approximate calculation of $p_i$ is made by formula 1.

$$p_i = p - p_p = p - RTm_p. \qquad . \qquad . \qquad . \quad (1)$$

$RT = 17033$ if pressures are expressed in mm. Hg at $0°$. $m_p =$ corrected concentration in g. mols. protein per litre of solvent in the protein solution. The estimation of molecular weights and corrected concentrations has been discussed by Adair and Robinson.[7]

Approximate calculations of the valence are made by the application of Donnan's [8] theory to the estimates of $p_i$ and measurements of the concentrations of diffusible ions in the dialysate, a solution of crystalloids in diffusion equilibrium with the protein solution.

## Membrane Potentials.

The suggestion that the valence of a colloidal electrolyte could be calculated from measurements of membrane potentials has been made by Bjerrum [9] and by Rinde.[10] Their measurements showed an anomaly observed by Hammarsten in that the observed osmotic pressures, representing the sum of the pressures due to the colloid and the diffusible ions is less than the pressure attributable to the diffusible ions alone. Linderstrøm-Lang [11] showed that the anomaly is correlated with the existence of considerable deviations from the ideal solution laws. In view of these deviations, estimations of the valences under such conditions must be regarded as apparent rather than real.

Adair and Adair [12] suggested that a better approximation to absolute values can be obtained if the membrane potentials measured are small. The type of apparatus required to minimise the sum of the experimental errors from all sources depends mainly on the concentration of salts in the dialysate. In very dilute solutions (0·001 $M$), it may be necessary to use an enclosed apparatus, and to maintain the hydrostatic pressure at the equilibrium value during the measurement, in order to minimise the electro-kinetic potentials, correlated with any movement of fluid across the membrane. In concentrated solutions of ions of unequal mobilities, special apparatus is required to obtain reproducible liquid junction potentials. A study has been made [12] of the sources of error with special reference to the range of concentration of electrolytes from 0·005 to 0·15 $M$. In the case of a number of solutions of colloidal electrolytes equilibrated with mixtures of salts within this range, the errors due to electrokinetic potentials may be unimportant, as shown by the agreement of the potentials calculated from hydrogen ion determinations

[6] Adair, *Roy. Soc. Proc. A.*, **108**, 627, 1925.
[7] Adair and Robinson, *Biochem. J.*, **24**, 1864, 1930.
[8] Donnan, *Z. Electrochem.*, **17**, 572, 1911.
[9] Bjerrum, *Z. physik. Chem.*, **110**, 656, 1924.
[10] Rinde, *Phil. Mag.*, **1** (7), 32, 1926.
[11] Linderstrøm-Lang, *Comptes Rend. Lab. Carlsberg*, **16**, No. 6, 1926.
[12] Adair and Adair, *Biochem. J.*, **28**, 199, 1934.

of the colloidal solution and its dialysate with direct measurements using collodion, cellophane and parchment membranes. It is possible to obtain constant and reproducible results with a smaller and simpler type of apparatus, in which the colloidal solution is not at the equilibrium pressure for the short period of time required for the potential readings. Rigid collodion membranes of 1·1 to 1·6 cm. diameter are filled with the colloidal solution and equilibrated at 0° with repeated changes of standard buffer solution, until the osmotic pressures and membrane potentials remain constant for several days. The upcurved tips of saturated potassium chloride calomel electrodes are dipped into the colloidal solution and the dialysate. The liquid junction is formed inside the tube in order to prevent contamination of the solutions with KCl over a period of time sufficient for the potential readings. Under favourable conditions, measurements of small potentials agree within 0·03 millivolts.

Measurements of membrane potentials of congo red made by this method are much larger than the earlier determinations of Azuma and Kameyama,[13] but these authors pointed out that in their apparatus includes a gelatine salt bridge, which may give a secondary "membrane potential," since the colloidal ion cannot diffuse into the gelatine.

Assuming that the conditions are favourable for the measurement of membrane potentials, the calculation of the valence is made by the application of formulæ 2, 3, 4 and 5. Since the solution as a whole is electrically neutral, the equivalent concentration of the colloidal ions must be determined by formula 2.

$$m_p n_p = S_- - S_+ \qquad . \qquad . \qquad . \qquad . \quad (2)$$

$n_p$ = mean valence of the colloidal ions. $S_-$ and $S_+$ denote the sums of the corrected equivalent concentrations of free diffusible anions $S_-$ and cations $S_+$. The concentrations of the ions in the dialysate are measured and estimates of the sums $S_-$ and $S_+$ are made by the application of formulæ 3 and 4.

$$r_i = a_i'/a_i'' = \text{antilog} - (n_i EF/2 \cdot 303 \times 10^3 \, RT) \qquad . \quad (3)$$

$r_i$ = ideal distribution ratio of a diffusible ion of valence $n_i$ between colloidal solution and dialysate. $a_i'$ = activity of an ion in the colloidal solution, $a_i''$ = activity in the dialysate. $n_i$ = valence. $E$ = membrane potential in millivolts. At 0°, $n_i EF/2 \cdot 303 \times 10^3 \, RT = n_i E/54 \cdot 16$.

$$m_i' f_i' = m_i'' f_i'' r_i \qquad . \qquad . \qquad . \qquad . \quad (4)$$

$m_i$ = corrected concentration of the free ion in g. mols. per litre of solvent in the colloidal solution. $f_i'$ = activity coefficient of the free ions. The terms with two accents refer to the dialysate, free from colloid, where the corrected concentration must be equal to the concentration in mols. per litre of solution.

If the membrane potential exceed 10 millivolts, there is a marked excess of ions inside the membrane, and according to the interionic attraction theory, the increase in ionic strength may reduce $f_i'$. If, however, the potential be below 2 millivolts, the difference between the ionic strengths is less marked. The assumption is made that when $E$ is small, $f_i''$ and $f_i'$ are equal.

A contracted method of calculation may be used, in which formula 3 is replaced by the exponential series. Omitting terms that are negligible when $E$ is below 2 millivolts, formula 5 is obtained.

[13] Azuma and Kameyama, *Phil. Mag.*, **50**, 1264, 1925.

$$n_p = (uJ/m_p)_0 = 0.0085 M\mu(E/C_v)_0 \qquad . \qquad . \qquad (5)$$

$u = EF/1000 \ RT = E/23.535$ at $0°$. $\mu =$ ionic strength $= \frac{1}{2}J$. $J =$ the sum of the concentrations of the ions in the dialysate multiplied by the squares of their valences. $M =$ molecular weight. $C_v =$ g. colloid per 100 ml. solvent. The subscripts refer to ratios estimated for an infinitely low concentration of colloid by extrapolation from a series of measurements where $C_v$ is varied but the concentration of the dialysate is kept constant.

Although the values of $n_p$ obtained by this method should give a better approximation to absolute values than the earlier methods referred to above, it must be recognised that there are two sources of error which cannot be eliminated by refinements in the technique for measuring small membrane potentials. In the first place, the elimination of errors due to liquid junction potentials may be incomplete ; in the second place, the assumption that $f_i'$ and $f_i''$ are equal when $E$ is small may be open to the following criticism. Formula 4 can be rearranged in the form $m_i' = m_i'' r_i + (f_i''/f_i' - 1)r_i m_i''$. If the ionic strength of the colloidal solution is high, $f_i'$ may be smaller than $f_i''$ and $m_i'$ may exceed $m_i'' r_i$. If the composition of the dialysate be constant and the concentration $m_p$ of the colloid be increased, the excess of free ions inside the membrane due to the effects of interionic forces must be some function of $m_p$, represented by the formula $m_i' = m_i'' r_i + b_2 m_p$, where $b_2$ is an undetermined coefficient representing the excess of free ions " attracted " by 1 mol. of colloid.

The corrected concentration of ions determined by chemical analyses is given by the formula 6.

$$m_i' \text{ (observed)} = m_i'' r_i + b_1 m_p + b_2 m_p \qquad . \qquad . \qquad (6)$$

$b_1 =$ g. equivalents of the ion combined with 1 g. mol. of the colloid.

It is evident that if $b_2$ approaches zero when $m_p$ is small, the effects of this term are eliminated when $n_p$ is determined by extrapolation as in formula 5. If $b_2$ approach a constant value, the correction is not eliminated by extrapolation, and $n_p$ corrected must be equal to $n_p$ observed $+ b_- - b_+$, where $b_+$ and $b_-$ represent the values of $b_2$ for the diffusible cations and anions, or the sum of these values if more than two species of ions be present in the dialysate. The correction is zero if $b_+$ and $b_-$ are equal, but it may be important if they are unequal.

In view of the possibilities of error due to the activity coefficients and the liquid junction potentials, it is necessary to devise methods for the experimental verification of formula 5. The measurement of membrane potentials over a wide range of concentrations has been recorded in a previous paper [12] and the results show that in all of the solutions of colloidal electrolytes investigated, the membrane potentials are represented by the empirical formula $E = kC_v$ where $k$ is a constant, when $E$ is less than 2 millivolts, a result in accordance with formula 5.

In the present investigation, it was found that the formula $m_i$ (observed) $= m_i'' r$ gives a close approximation to the distribution of the anion $HCO_3$ in mixtures of $0.02 \ M$ sodium bicarbonate and congo red, and a fair approximation to the distribution of the cations K, Na and $NH_4$, when solutions of proteins, including hæmoglobin and serum albumin are equilibrated with a number of dialysates containing from $0.015$ to $0.05$ equivalents of these cations. It may be inferred that both of the terms $b_1$ and $b_2$ are small. On the other hand $m_i'$ (observed) may be much greater than the calculated value $m_i'' r_i$ in the case of the

cation Na in the solutions of congo red, and in the case of the anions Cl, $HCO_3$, $H_2PO_4$ and $HPO_4$, when the colloidal electrolyte is a protein. Even if the protein be at the isoelectric point or in the region of the isoelectric point, there is a marked excess of anions inside the membrane.

Values of $(b_1 + b_2)$ recorded in Table I. are calculated by formula 6 from distribution measurements obtained from sheep hæmoglobin with a low valence $n_p = + 0.3$, equilibrated at 0° with a mixture of 0.0045 $M . (NH_4)_2HPO_4 + 0.0053 \ M . NH_4H_2PO_4$, where the $p_H$ value is 7 and the ionic strength 0.0188.

TABLE I.

| $m$ (hæmoglobin)    .        | 0.00558 | 0.00446 | 0.00240 | 0.00216 | 0.00125 | 0.00065 |
|------------------------------|---------|---------|---------|---------|---------|---------|
| $(b_1 + b_2)$ phosphate .    | 4.3     | 3.4     | 4.3     | 3.9     | 4.8     | 4.4     |
| $(b_1 + b_2)$ ammonium.      | 0.4     | 0.4     | 0.5     | 0.4     | 0.0     | —       |

It will be seen that $(b_1 + b_2)$ is approximately constant, and markedly different for anions and for cations. Since there is no tendency for $(b_1 + b_2)$ to diminish as $m_p$ is reduced, the experiments cannot be reconciled with formula 5 unless the excess of ions be attributed to combination rather than attraction. This hypothesis is not improbable, because the interionic forces should influence the distribution of cations as well as of anions, whereas the effects of chemical forces are more specific.

Table II. gives the apparent valences of three colloidal electrolytes, determined by osmotic methods for comparison with the results obtained by measurements of the membrane potentials. Values of $n_p$ estimated by osmotic methods are relatively low, except in the case of congo red, but the effects of interionic forces, neglected in the calculations, tend to give low results.

TABLE II.—DETERMINATIONS OF VALENCE AND APPARENT VALENCES BY DIFFERENT METHODS.   TEMPERATURE 0°.

| Colloid. | Molecular Weight. | Dialysate. | Ionic Strength. | Membrane Potential. $n_p$. | Osmotic. $n_p$. | Acid Combined. $y$. |
|----------|-------------------|------------|-----------------|----------------------------|-----------------|---------------------|
| Congo red .        . | 696    | $NaHCO_3$   | 0.02 | − 1  | − 1  | − 2  |
| Edestin    .        . | 17,000 | HCl         | 0.01 | + 25 | + 19 | + 27 |
| Serum albumin  .      | 72,000 | $NH_4, PO_4$ | 0.02 | − 12 | − 10 | − 9  |
| Serum albumin  .      | 72,000 | $NH_4, PO_4$ | 0.04 | − 14 | − 11 | − 8  |

Values for $y$, the total acid or base combined with the colloid, usually exceed the values of $n_p$, a result which may be attributed to the term $b_1$. In the case of serum albumin, $n_p$ is greater [12] than $y$. This difference can be accounted for if a reaction of the type formulated below can take place.

$$^+Pr^- + NH_4^+ + H_2PO_4^- = [Pr . H_2PO_4]^- + NH_4^+$$
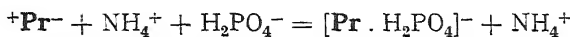
$^+Pr^-$ represents a zwitterion.

The values of $n_p = - 12$ and $- 14$, recorded for serum albumin, are " apparent values " for two solutions where the membrane potentials exceed 12 millivolts. The experimental data recorded in a previous paper show that $n_p = - 17.1$ in the more dilute phosphate mixture when $m_p$ approaches O.

TABLE III.—DETERMINATIONS OF RATES OF CHANGE OF VALENCE AND ACID
   COMBINED.   HORSE SERUM ALBUMIN AND SHEEP CO HÆMOGLOBIN, MOL.
   WT. 67,000.  $p_H$ VALUES IN ISOELECTRIC REGION.   $\mu = 0.02$.

| Colloid. | Dialysate. | Valence Increment by Membrane Potentials at 0°. $\beta$. | Valence Increment (Apparent) by Cataphoresis at 20°. | Buffer Value. $\beta$. |
|---|---|---|---|---|
| Serum albumin  . | Na . Acetate | 13 | 3·8 | 20 |
| Hæmoglobin      . | Na, PO$_4$ | 4 | 2·9 | 8 |

Table III. gives values of the valence increment $\beta_n$ and the buffer value $\beta_H$ defined by the formulæ

$$\beta_n = - \left(\partial n_p / \partial p_H\right)_\mu. \quad \beta_H = \partial y / \partial p_H.$$

The symbol $\mu$, representing the ionic strength of the dialysate, is constant. Table III. shows that $\beta_n$ is less than $\beta_H$. This conclusion is of importance in connection with Abramson's method for calculating valences.[5] No direct measurements of $\beta_n$ were available when his work was published, and his empirical formula correlating valences and mobilities of colloids is based on the assumption that the buffer value $\beta_H$ is the same as $\beta_n$. It will be seen that $\beta_n$ exceeds the apparent value calculated as described by Tiselius,[3] but, as he has pointed out, these apparent values may require multiplication by a numerical factor of 2 or more, on account of the effects of the interionic forces described by Debye and Hückel.[2]

## Summary.

Estimates of the apparent valence of colloidal ions made by different methods are not identical, on account of interionic forces and the combination of ions with the colloidal particles, although approximate agreement is obtained under certain conditions. It is suggested that of the methods now available, the best approximation towards the elimination of errors is obtained when the calculations are based on measurements of membrane potentials, in a range of concentrations where the potentials are small, and the limiting value for very low concentrations of colloid are obtained by extrapolation, from a series of measurements where the composition of the dialysate is kept constant.
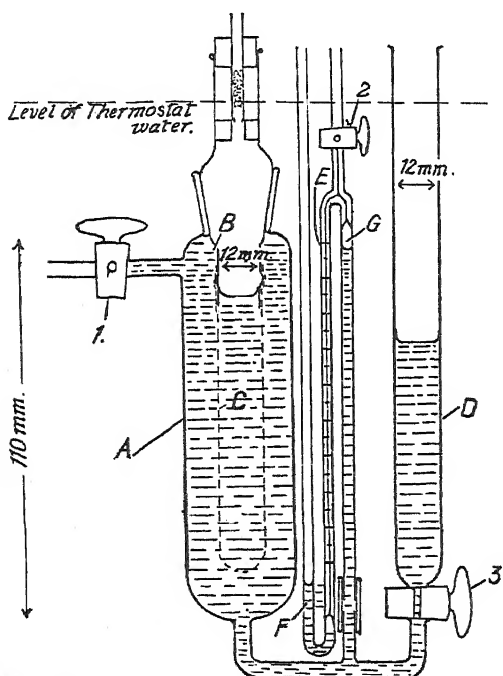
*From the Physiological Laboratory,*
    *Cambridge.*

# A NEW TYPE OF OSMOMETER FOR LOW PRESSURES, WITH SOME PRELIMINARY RESULTS FOR GUM ARABIC.

By Henry Bowen Oakley.

In order to calculate the mean molecular weight of colloids from measurements of osmotic pressure some form of extrapolation to infinite dilution always has to be employed. The uncertainty of this extrapolation is greatly diminished if measurements can be made at concentrations sufficiently low for the Van't Hoff law to be valid. The higher the molecular weight the lower will be the osmotic pressure in the range where this law holds, so that it may become essential to measure accurately pressures of less than ten millimetres of water if any reliance is to be placed on the extrapolation, and an accuracy of 0·1 mm. pressure should be striven for.

It appeared to the author that the chief source of error of any of the usual forms of osmometer using either a capillary manometer or depending on the measurement of the level of a liquid in a capillary, lies in the uncertainty of the correction for the capillary rise of a liquid in such tubes. This being especially so for many colloidal solutions.



A Outer vessel containing solvent.
B Tube with ground glass joint carrying collodion sac C containing colloid.
D Outer levelling tube of same diameter as B, with tap 3.
E S-shaped capillary 0·2 mm. diameter with scale and wider tubes each end.
F Alcohol.
G Air space between alcohol and outer solution.
1 and 2 are taps used for filling or changing the solution in A.

Fig. 1.—Osmometer for low pressures.

The use of wider tubing no doubt reduces this uncertainty ; but, to reduce the correction to less than a millimetre, the diameter of the tube has to be nearly one centimetre and the time required to reach equilibrium is correspondingly lengthened.

Unless one is prepared to work at 0° as Adair[1] recommends, the time required to establish equilibrium is often an important factor when the colloid is liable to bacterial decomposition as is gum arabic. Furthermore if the osmometer is capable of indicating fairly rapid changes in osmotic pressure, very valuable information can often be obtained concerning the presence of impurities or decomposition products towards which the membrane may be less permeable than towards water.

A form of osmometer described by Buchner and Samwel[2] was first tried, but it was found that the flat membrane could not be made sufficiently rigid even after the introduction of wire gauze on both sides.

The various difficulties have been overcome in a highly satisfactory manner by using the osmometer indicated in Fig. 1.

The colloidon sacs were prepared by pouring collodion (about 4 per cent. solution in 60 : 40 ether-alcohol) into a test-tube and draining off the solution and allowing to dry about fifteen minutes ; in this way four or five coats were applied and the sac was finally removed by immersing in water. Although these sacs seemed perfectly satisfactory for this work, they are very much thicker near the mouth than at the base. A stronger and more uniform sac of finer permeability if necessary can be prepared by the method described by Adair.[1]

### Description of Osmometer.

The colloid solution in the collodion sac C is open to atmospheric pressure, while rapid evaporation is prevented by a narrow tube plugged with cotton wool.

Water flows by osmosis from A through the membrane into C and when tap 3 is closed the meniscus at G falls and consequently the alcohol at F is drawn up the capillary E. This continues until the negative pressure exerted by the column of alcohol in the capillary balances the osmotic "suction" of C.

The pressure corresponding to this equilibrium position of the alcohol meniscus is obtained by opening tap 3 and taking a series of readings of the difference of levels of the menisci in B and D with a cathetometer, by adding or withdrawing liquid from D by means of a drawn out pipette; the corresponding readings of the alcohol meniscus in the capillary are read off on the attached scale with the aid of a magnifying glass. The equilibrium pressure (in terms of millimetres of the solution in A at 25°) is then obtained by graphical interpolation. Alcohol was used rather than water because of its low viscosity and surface tension which eliminated any tendency to "sticking" in the capillary.

The advantages of this procedure are that it is possible to obtain the high sensitivity and rapidity of establishment of equilibrium associated with a very fine capillary manometer while at the same time practically eliminating the uncertainty of the capillary correction, since tubes D and B are wide and of the same diameter.

A further advantage lies in being able to withdraw portions of the colloid solution for analysis, and, by adding solvent or the appropriate solution and mixing by bubbling air through, to make a whole series of determinations at different concentrations with a small sample.

It was found that so far as the water equilibrium was concerned this was established in less than an hour, that the equilibrium of electrolytes might take three or four hours, and that the establishment of equilibrium with diffusible organic impurities in gum arabic might take two or more days.

[1] Adair, G. S., *Proc. Roy. Soc.*, **108A**, 627, 1925.
[2] Buchner, E. H. and Samwel, P. J. P., " The Colloid Aspects of Textile Materials and Related Topics," Faraday Soc. Discussion, p. 32, 1932.

When a slow chemical reaction was proceeding, as, for instance, the hydrolysis of the gum by $N/50$ HCl, equilibrium may not be reached, but analysis of the sample and of the dialysate may yet give the true concentrations at the particular osmotic pressure chosen provided that the chemical reaction is slow enough. In other cases a displacement of the alcohol capillary meniscus of 2 mm. from its equilibrium position required only about ten minutes for its return.

It was usually found that after disturbing the alcohol meniscus for the purpose of adjusting the level in D it returned only to within a few tenths of a millimetre *below* its initial position in half an hour. It was thought that the slightly higher value was due to an increase of the surface tension of the alcohol due to the condensation of water vapour on to the surface layer and that on moving the meniscus this layer becomes mixed with the alcohol beneath and the surface tension falls again. For this reason a second intrapolation was made in which the alcohol meniscus was only moved 1 or 2 mm. and afterwards another reading of its equilibrium position within half an hour was taken to be the one most applicable to the interpolation curve.

The temperature control of the thermostat is important. The regular fluctuation of $1/25°$ produced a regular movement of 0·6 mm. in the alcohol meniscus and the mean position was taken. The greater part of the measurements recorded in this paper were made in hot weather while the room temperature was such as to allow a very much finer temperature control.

## Experiments with Gum Arabic.

Gum Arabic or Gum Acacia was one of the substances classed as a true colloid by Graham [3] in 1862. Its constitution was investigated by O'Sullivan [4] in 1884 and earlier by Neubauer [5] and Gelis [6] and others.

These investigators clearly recognised the substance as being a mixture of the calcium and magnesium salts of an acid of well-defined composition. Recent work on its constitution has been done by Norman [7] and by Butler and Cretcher.[8] The growth of colloid chemistry served rather to obscure its chemical nature until in 1931 we find Taft and Malin [9] denying that it can be a colloid because they rediscovered its relationship to an organic acid.

The gum is a carbohydrate, Norman states that the only sugars it contains are arabinose and galactose and gives the following composition :—

| | | |
|---|---|---|
| Uronic acid anhydride . | . 17·6 per cent. | |
| Anhydro-arabinose . | . 20·5 ,, ,, | |
| Anhydro-galactose . | . 61·9 ,, ,, | |

By hydrolysis in 3 per cent. boiling sulphuric acid this investigator has shown that the arabinose is very much more easily split off than the galactose, this result is of significance when we come to consider the dialysis and osmotic pressure results of electrolialysed gum. The linkage of the arabinose is considered to be of a glucosidic (ethereal) nature.

In 1928 Thomas and Murray [10] investigated the osmotic pressure

[3] Graham, T., *Chem. Soc. Trans.*, **15**, 257, 1862.
[4] O'Sullivan, *Chem. Soc. Trans.*, **45**, 41. 1884.
[5] Neubauer, *Chem. Soc. Trans.*, 624, 1854.
[6] Gelis, *Chem. Soc. Trans.*, 496, 1857.
[7] Norman, *Biochemical Journ.*, **23**, 524, 1929.
[8] Butler and Cretcher, *J.A.C.S.*, **51**, 1519, 1929.
[9] Taft and Malin, *J. Phys. Chem.*,, **35**, 874, 1931.
[10] Thomas and Murray, *J. Phys. Chem.*, **32**, 676, 1928.

and membrane equilibria of the gum and also showed by electro-titration that it behaved like a comparatively strong acid. They obtained semi-quantitative agreement with the simple theory of the Donnan membrane equilibrium. They made, however, no attempt to calculate the mean molecular weight from their measurements.

The viscosity with and without the addition of salts has been investigated by a number of workers. Kruyt and Tendeloo,[11] in particular, have shown that there is no structural viscosity effect, a conclusion which is disputed by Ostwald [12] at any rate for the more concentrated solutions.

Pauli and Ripper [13] investigated the hydrogen ion concentration and conductivity of the electrodialysed gum and also the membrane equilibria of the silver compound, but they made no measurements of the osmotic pressure with a view to calculating the molecular weight. Taft and Malin [9] have made measurements of the viscosity, density and freezing-point of solutions of undialysed gum. D. R. Briggs [14] also investigated the membrane equilibria and osmotic pressure of the gum with sodium and calcium chloride solutions and, basing his calculations on measurements of the $p_H$ on both sides of the membrane, found that the osmotic pressure calculated from the difference of ionic concentrations was much greater than that observed, a result also recorded by Thomas and Murray.[10] He called this difference the anomalous osmotic pressure of the gum.

Numerous determinations of the osmotic pressure have also been made for medical purposes, amongst which may be mentioned those of Dodds and Haines [15] and of Krogh and Nakazawa,[16] but as these are only concerned with rather rough measurements on the crude gum at a concentration of about 6 per cent. they need not concern us.

Finally de Jong [17] has determined the equivalent weight of the acid, sodium, ammonium and strontium gums and finds a mean value of 1210 in connection with extensive studies on coacervation.

It is thus apparent that a systematic investigation of the osmotic pressure of the acid gum and of its compounds with different bases under conditions which will allow one to estimate the constancy or otherwise of the mean molecular weight, is a first requisite in an extended investigation which aims at using this substance as a means of elucidating some of the problems of colloidal electrolytes of a high valence type.

In this paper the terms acid gum, sodium gum, etc., will be used rather than arabic acid, sodium arabate, because the latter have already been employed to denote one of the acid products of hydrolysis.

## Preparation of Materials.

Acid gum.—It was found that solutions of the gum were very liable to attack by *bacillus subtilis*, and unboiled preparations, although covered with a layer of toluene and kept in a refrigerator developed a marked cloudiness due to this bacillus after two or three weeks. The initial solution of the crude gum was therefore always boiled for fifteen minutes ;

[11] Kruyt and Tendeloo, *Koll. Beih.*, **29**, 396, 1929.
[12] Ostwald, Auerbach, Feldmann, Trakes and Malss, *Koll. Zeitschr.*, **67**, 211, 1934.
[13] Pauli, Wo. and Ripper, E., *Koll. Zeit.*, **62**, 162, 1933.
[14] Briggs, D. R., *Symposium on Quantitative Biology, Cold Spring Harbor*, **I**, 152, 1933.
[15] Dodds and Haines, *Biochem. Journ.*, **28**, 499, 1934.
[16] Krogh and Nakazawa, *Biochem. Zeit.*, **188**, 241, 1927.
[17] H. G. Bungenberg de Jong, *Biochem. Z.*, **262**, 160, 1933.

in some cases the purified gum solution was again boiled before storing in the refrigerator. It was thought advisable to prepare only small quantities of stock solutions at a time (about 50 c.c. of 5 per cent. to 10 per cent solutions).

Fifty c.c. of a 10 per cent solution of the crude gum, after boiling and cooling was acidified with 5 c.c. glacial acetic acid and enough (95 per cent.) alcohol added in a slow stream with vigorous stirring to cause an initial slight precipitation. The solution was then centrifuged and decanted, this removed dirt and mucilage. A further addition of alcohol was made to cause a copious precipitate and this was separated by centrifuging and dissolved in warm water. The gum was again precipitated by alcohol and dissolved in 100 c.c. of water. This solution was then electro dialysed for twenty-four to thirty hours in a small Pauli type dialyser fitted with platinum gauze electrodes. A layer of toluene was poured over the surface of the solution, which was stirred by bubbling through nitrogen from a cylinder washed in dilute nitric acid to remove ammonia. The anode membrane was of parchment paper and the cathode membrane of cellophane, both membranes being clamped between a pair of cellophane washers.

This arrangement prevents the solution being diluted by electroosmosis ; another advantage is that the cellophane is more resistant than collodion to the alkaline solution formed at the cathode. All three compartments of the dialyser were cooled by allowing water to drip on to strips of cloth laid over the glass vessels. Immersing the whole dialyser in running water was found to be unsatisfactory owing to electrical leakage at the junctions of the membranes through the cooling water. The main voltage of 240 volts was applied in series with a resistance in the early stages of dialysis.

The gum thus prepared had less than 0·05 per cent. of ash. A 3 per cent. solution had a specific conductivity of $1·1 \times 10^{-3}$ mhos. at 25° which agrees with Pauli and Ripper's [13] figures.

Titration with $N/20$ Baryta using phenol phthalein as indicator gave an equivalent weight of 1189. By electrometric titration Thomas and Murray [10] obtained a value of 1177, Brigg's [14] figure is 1176 and O'Sullivan's [4] 1276.

Half of this solution was again boiled and portions of the boiled and unboiled solutions were neutralised with $N/10$ caustic soda, using methyl red as indicator.

## Osmotic Pressure of Sodium Gum against $N/10$ NaCl.

A succession of dilutions were made *in situ* in the osmometer ; the time required to establish osmotic equilibrium was very much longer for the first solution (two or three days) than for subsequent dilutions (ten hours).

This is due to a low molecular weight constituent diffusing through the membrane and taking some time to reach equilibrium on both sides. The concentrations were determined by evaporating to dryness on a steam bath weighed portions of the solution withdrawn from the osmometer, and then heating for one and a half to two hours at 100° in a vacuum desiccator. The heat was applied by an electrically heated bath of Wood's metal.

The residue contains, in addition to the sodium gum, sodium chloride. In the experiments recorded in Fig. 1 for unboiled gum it was assumed that the concentration of the sodium chloride (per 100 grms. water) was the same on both sides of the membrane. A correction for its weight was calculated from the concentration of NaCl in the dialysate which was analysed at the end of the series of measurements.

The concentrations of gum for the boiled sample were corrected for NaCl by direct analyses of the residues for sodium by ignition with $H_2SO_4$

and weighing as sulphate, allowance being made for the sodium combined with the gum.

The curves in Fig. 2 show that the osmotic pressure of the boiled sample lies some 3 per cent. higher than that of the unboiled sample.

The ideal straight line relationship between pressure and concentration only begins to hold for solutions below 1 per cent. This is better illustrated by Fig. 2 where the ratio $P/C$ is plotted against concentration.

The interpretation of these and other results in terms of the molecular weight will be reserved until the end of the paper.

### Experiments with Acid Gum. Hydrolysis.

When electro-dialysed gum is dialysed against water the osmotic pressure rises to a maximum and then slowly falls to a lower constant value. With successive changes of water increasingly higher maxima are reached and the lower constant values more nearly approach the maxima until further changes of water produce no further increase of osmotic pressure. For a concentration of gum initially 1 per cent. the maximum pressure attained in two experiments was 328 mm. of water.

If at this stage the water is replaced by $N/50$ HCl the pressure immediately falls to about 9·5 mm. and then slowly to 8 mm.



+ Boiled sodium gum in $N/10$ NaCl.
⊙ Unboiled sodium gum in $N/10$ NaCl.
△ Boiled acid gum in $N/50$ HCl.

FIG. 2.

If on the other hand a 1 per cent. solution of gum is dialysed from the start against $N/50$ HCl the pressure rapidly adjusts itself to about 14 mm. but falls to 9·5 mm. in about four hours and then slowly to about 8 mm.

These changes are accompanied by the passage through the membrane of organic constituents as is shown by Table I.

It is evident that the electrodialysed gum contains about 8 per cent. of diffusible acid constituents whose average equivalent weight is about
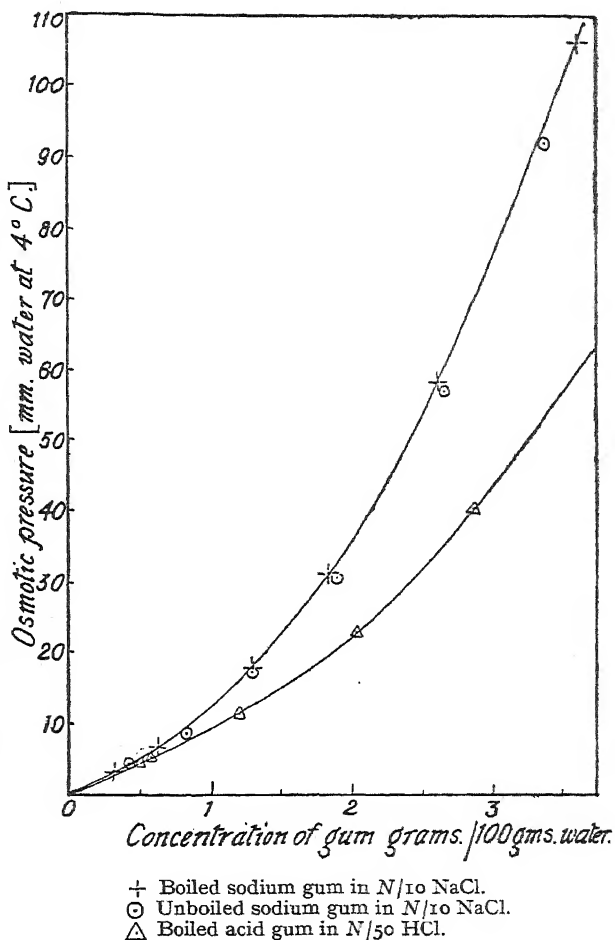
the same as that of the gum itself. It is the presence of this acidic constituent which depresses the osmotic pressure of the gum when measured against water, and its gradual removal allows the true osmotic pressure



+ Boiled sodium gum in $N/10$ NaCl.
⊙ Unboiled sodium gum in $N/10$ NaCl.
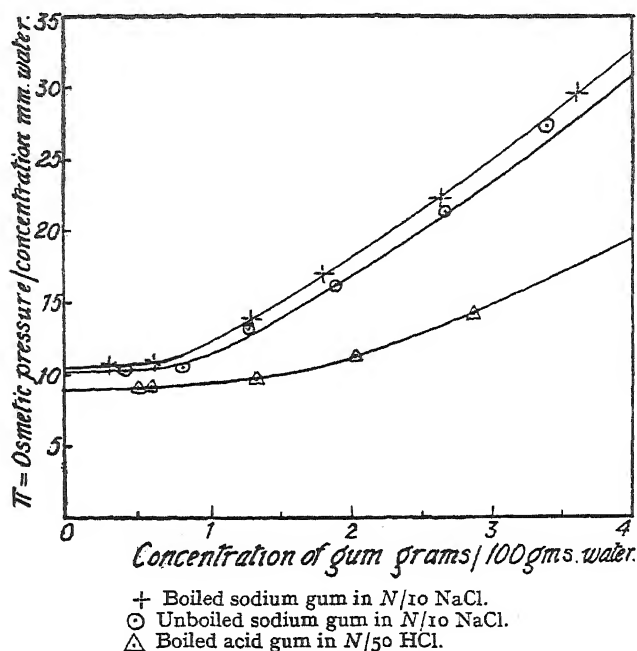△ Boiled acid gum in $N/50$ HCl.

FIG. 3.

of the acid gum to be exerted. Furthermore this constituent is presumably responsible for the temporary pressure of 14 mm. in $N/50$ HCl, since the gum from which it has been removed by dialysis immediately shows a pressure of 9·5 mm.

TABLE I.—DIALYSIS OF ELECTRODIALYSED GUM ARABIC. TOTAL GUM ADDED, 0·2993 G. FINAL CONCENTRATION, 1·652 G./100 G. $H_2O$.

| Time Interval Between Changes of Outer Liquid. | Weight of Residue in Dialysate. | Per Cent. of Total Gum Found in Dialysate. | $N/10$ Alkali to Neutralise Dialysate. c.c. | Equivalent Weight of Diffusate. |
|---|---|---|---|---|
| **A. Against Water.** | | | | |
| 20 hours | 15·0 mg. | 5·01 | 0·17 | 880 |
| 22 ,, | 4·8 ,, | 1·61 | 0·04 | 1200 |
| 72 ,, | 3·3 ,, | 1·10 | 0·025 | 1300 |
| 22 ,, | 0·5 ,, | 0·17 | Total 7·9 per cent. | — |
| **B. Against $N/50$ HCl.** | | | | |
| 23 hours | 23·0 mg. | 7·68 | — | — |
| 24 ,, | 14·8 ,, | 4·95 | — | — |
| 24 ,, | 9·6 ,, | 3·21 | — | — |
| 31 ,, | 8·8 ,, | 2·93 | — | — |
| 39 ,, | 7·4 ,, | 2·48 | Total 21·2 per cent. | — |

The fact that Thomas and Murray [10] also report a pressure of 14 mm. for their electrodialysed gum in acid solutions seems to suggest that only the temporary equilibrium point was measured by them and that we are

dealing with an equilibrium mixture between the acid gum and its products of auto-hydrolysis.

The addition of $N/50$ HCl further hydrolyses the gum, but instead of this proceeding at a constant rate for each change of acid, the amount of dialysable products fall to about a quarter of their initial rate of production in six days, when 21 per cent. of the gum has been hydrolysed. This hydrolysis accounts for the slow decrease of osmotic pressure from 9·5 to 8 mm.

It appears either that a certain fraction of the gum is more easily hydrolysed than the remainder, or else, if the gum is a homogeneous substance, one hydrolysis reaction outstrips any other. From Norman's results mentioned earlier the latter hypothesis seems to be the true one ; the other investigators have assumed that dilute acid causes no hydrolysis.
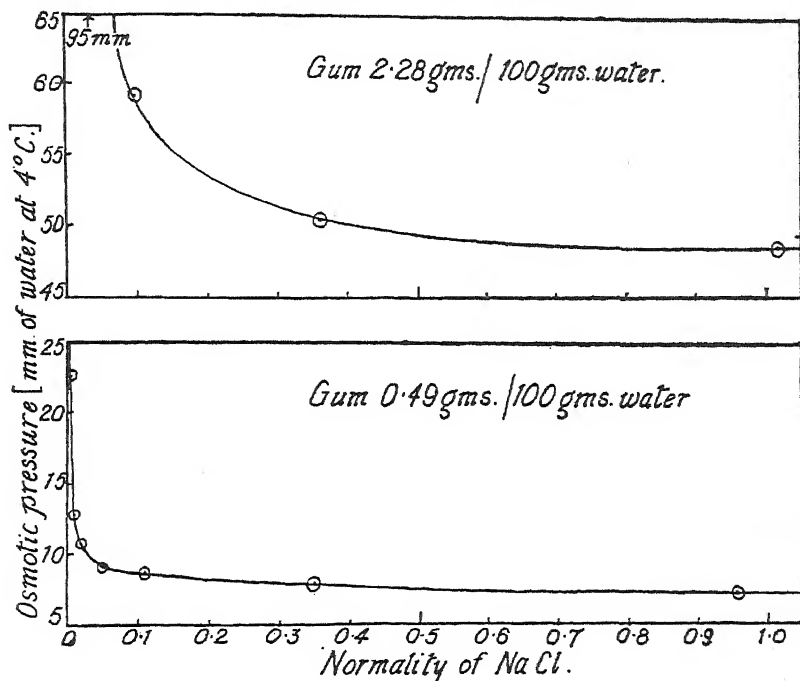


FIG. 4.

## Osmotic Pressure of Acid Gum.

In Fig. 2 is given the osmotic pressure of electrodialysed gum against $N/50$ HCl. Corrections to the concentration of the gum were applied for the products of hydrolysis. Three days were allowed before the first measurement at the highest concentration was made so that the initial rapid hydrolysis was at an end. This amounted to about 30 per cent. of the gum initially added which corresponds well with the total of 29 per cent. removed by dialysis in Table I.

Samples of gum solution for determination of the concentration were neutralised with $N/10$ NaOH before drying to prevent decomposition by the HCl. A correction was then applied for the NaCl present. The limiting values for $P/C$ (Fig. 3) are 10 to 15 per cent. lower than those of the sodium arabate. This may be due to the imperfect stability of the gum in acid solution or to a larger particle size, or to a more efficient suppression of the ion pressure difference by $N/50$ HCl than by $N/10$ NaCl,

the much lower values of the osmotic pressure at higher concentrations of the acid gum compared with those for sodium compound would support this view. Furthermore the next experiment shows that $N/10$ NaCl is insufficient to suppress the osmotic pressure to its minimum value.

TABLE II.—$P/C$ FOR SODIUM GUM AT DIFFERENT CONCENTRATIONS OF NaCl IN MM. WATER AT $4°$.

| C = 0·49. | | C = 2·28 g./100 g. Water. | |
|---|---|---|---|
| Normality, NaCl. | $P/C$. | Normality, NaCl. | $P/C$. |
| 0·96 | 14·7 | 1·02 | 21·3 |
| 0·35 | 16·3 | 0·36 | 22·2 |
| 0·11 | 17·8 | 0·095 | 26·0 |
| 0·049 | 18·6 | 0·035 | 41·5 |
| 0·020 | 21·8 | — | — |
| 0·011 | 26·2 | — | — |
| 0·0039 | 46·2 | — | — |

## Osmotic Pressure of Sodium Gum at Different Concentrations of NaCl.

For this experiment a sample of sodium arabate was used which was prepared from gum which had not been electro-dialysed or treated with acid. The crude gum was twice precipitated from $N/10$ NaCl solution with alcohol and was then dialysed at $0°$ for three weeks against frequent changes of $N/10$ NaCl.

The results for two concentrations of gum are shown in Table II. and Fig. 4. It is seen that the ratio $P/C$ continues to decrease considerably at concentrations of NaCl higher than $N/10$, and that this applies to the 0·5 per cent. solution as well as to that of higher concentration.

A striking feature of the results is that at 0·1 $N$. NaCl the ratio $P/C$ is 17·8 while the corresponding value for the sodium compound prepared by neutralising the electro-dialysed gum is only about 10·5.

## Osmotic Pressure of Calcium Gum Against $N/10$CaCl$_2$.

In this experiment also non-electro-dialysed gum was used, the preparation being analogous to that of the previous experiment.

Table III gives the results.

The value of $P/C$ while tending towards a constant is only 11·5 compared with the lowest value (14·7) obtained for the sodium gum in $N$. NaCl. This may be due to aggregation of the calcium gum particles but in my opinion it is more likely to be due to the more efficient suppression of the ionic pressure difference by the di-valent calcium ions.

TABLE III.—CALCIUM GUM IN 0·084 $N$. CaCl$_2$.

| C. | P. | P/C. |
|---|---|---|
| 2·56 | 42·5 | 16·6 |
| 1·54 | 24·6 | 16·0 |
| 1·04 | 12·6 | 12·1 |
| 1·03 | 11·9 | 11·6 |
| 0·875 | 10·3 | 11·8 |
| 0·529 | 6·05 | 11·5 |

## Calculation of Mean Molecular Weights.

According to Adair [17] when the relationship between $P$ and $C$ approximates to a straight line at low concentrations, i.e. when $P/C$ approaches a constant value, then if this ratio is extrapolated to $C = 0$ the molecular weight is given by the following equation :

$$M = 10 \ RT/\pi_0$$

where $M$ = molecular weight, $R$ and $T$ have their usual significance and $\pi_0 = P/C$ when $C = 0$, and $C$ = grams of dry colloid in 100 c.c. of solution. According to Donnan [18] $C$ should be the mass per 100 c.c.

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[17] Adair and Robinson, *Biochem. J.*, **24**, 1864, 1930.
[18] Donnan, F. G., *this Vol.*, 80.

of water added to make up the solution, and the constancy of $\pi$ is evidence that the added electrolyte is of sufficient concentration to suppress the ion pressure difference on both sides of the membrane. The value of $C$ used here is that defined by Donnan except that weight concentrations are used which at 25° makes $\pi$ 0·3 per cent. too low. In the table which follows it has also been assumed that the values of $\pi$ for the non-electrodialysed sodium gum at a concentration of 0·49 per cent. and with a concentration of NaCl not lower than 0·1 (Table II.) follow the same extrapolation to $C = 0$ as the electrodialysed sodium gum. This extrapolation has been made graphically.

It is clear that on any interpretation the electrodialysed sodium gum has a mean molecular weight some 70 per cent. higher than the non-electrodialysed gum. The large discrepancies of the apparent molecular weight of either of the two samples may be accounted for in two different ways. Either one may assume that the aggregation of the gum particles varies under the different experimental conditions, in which case there is little more to be said; or else one may regard the constancy of $P/C$ at low concentrations as making the aggregation hypothesis improbable. The variations may then be ascribed to varying degrees of suppression of the ionic pressure difference.

### TABLE IV.—APPARENT MEAN MOLECULAR WEIGHTS OF GUM PREPARATIONS.

| Description. | Electrolyte. | $\pi_0$. | Mol. Wt. |
|---|---|---|---|
| **A. Electro-dialysed Gum.** | | | |
| Boiled Na-gum . | $N/10$ NaCl | 10·3 | 245,000 |
| Unboiled Na-gum | $N/10$ NaCl | 10·0 | 252,000 |
| Boiled H-gum . | $N/50$ HCl | 8·8 | 286,000 |
| **B. Non-electro-dialysed Gum.** | | | |
| Na-gum . . | 0·11 $N$ NaCl | 17·4 | 152,000 |
| | 0·35 $N$ NaCl | 15·9 | 158,000 |
| | 0·96 $N$ NaCl | 14·4 | 175,000 |
| Ca-gum . . | 0·084 $N$ CaCl$_2$ | 11·2 | 225,000 |

The calcium gum in $N/10$ CaCl$_2$ would then give the value nearest to the true molecular weight of one sample and the acid gum in $N/50$ HCl the best value for the electro-dialysed and partially hydrolysed gum, although we have no evidence that even here the ionic pressure difference is completely suppressed.

Fortunately Adair and Adair [19] have recently shown how the measurement of membrane potentials may be made to correct for this source of error and this method will have to be applied before further advance can be made.

If this proves to be the source of the discrepancies then the opinion that approximate constancy of $P/C$ at low concentration is necessarily a criterion for the elimination of the ion pressure difference will have to be modified. It is probably true only for molecules of low charge or valency such as proteins near their iso-electric point.

## A Provisional Estimate of Some of the Chemical Constants of Gum Arabic.

In spite of the uncertainty of the molecular weight of the gum it is of interest to calculate provisional figures for such quantities as valency

[19] Adair, G. S., and Adair, M. E., *Biochem. Journ.*, **28**, 199, 1934.

and apparent degree of ionisation. For this purpose we will consider the acid gum and take the figure 290,000 as its molecular weight. The following symbols will be used. $M$ = molecular weight; $E$ = equivalent weight; $n_c$ = maximum valency; $n_e$ = effective valency; $C_H$ = hydrogen ion concentration; $P_w$ = osmotic pressure against water; $P_{(HCl)}$ = osmotic pressure against $N/50$ HCl in mm. of water; $C$ = concentration of gum in grams per 100 grams of water; $C_E$ = equivalent concentration of gum = 10 $C/E$, $\pi_w = P_w/C$. $\alpha$ = percentage ionisation. Then we have the following relationships :

$$n_c = M/E, \quad n_e = \pi_w/\pi_{0(HCl)} - 1, \quad \alpha_P = n_e/n_c$$

and also $\alpha_H = C_H/C_E$ from $p_H$ measurements, the latter have been taken from Pauli and Rippers [13] figures. The following table gives these values for $E = 1200$ :—

| $C$. | $P_w$. | $\pi_w$. | $\pi_0$ (HCl). | $n_e$. | $n_c$. | $\alpha_P$. | $C_H$ | $C_E$. | $\alpha_H$. |
|------|--------|----------|----------------|--------|--------|-------------|-------|--------|-------------|
| 1·00 | 365    | 365      | 8·8            | 40     | 240    | 16·6        | 0·00186 | 0·00833 | 22·3 |
| 1·65 | 566    | 343      | 8·8            | 38     | 240    | 15·8        | 0·00290 | 0·0137  | 21·2 |

No very definite meaning can be attached to the figures for ionisation since, as noted by Pauli and Ripper, the measurements are really activities and it is probable that these are not constant and differ considerably from unity. The much lower values obtained by the osmotic method may be due to experimental error since very small traces of electrolyte will have a very strong depressing effect on the osmotic pressure and the acid gum may be giving uronic acid continuously by auto-hydrolysis. Alternatively there may be a systematic error in the $p_H$ measurements since the elimination of liquid junction potentials is far from certain with colloids.

## Summary.

1. An osmometer has been described capable of measuring pressures of a few millimetres or more of water with an accuracy of 0·1 mm.

2. Osmotic pressures at 25° have been measured of solutions of gum arabic preparations over a range of $\frac{1}{2}$ per cent. to $3\frac{1}{2}$ per cent. concentration.

3. The sodium gum prepared by neutralising the electrodialysed preparation appears to have a molecular weight some 70 per cent. higher than the analogous compound prepared without electrodialysis.

4. Evidence is presented which favours the hypothesis that the acid electrodialysed gum is an equilibrium mixture with its products of auto-hydrolysis, and that $N/50$ HCl causes two parallel hydrolysis reactions, one of which proceeds to completion much more rapidly than the other.

5. Curves are presented showing the fall of osmotic pressure of the sodium gum when the concentration of NaCl increases from $N/300$ to $N/1$. This decrease appears to be continuous up to normal concentrations and is attributed to progressive suppression of the ionic pressure difference.

6. Calcium chloride and hydrochloric acid produce much larger depressions of osmotic pressure than sodium chloride and this is attributed to a more complete suppression of the ionic pressure difference.

7. Provisional estimates of some chemical constants for the electrodialysed gum give the following results. Equivalent weight 1200, molecular

weight 290,000, maximum valency 240, effective valency in 1 per cent. solution 40.

I wish to thank Professor F. G. Donnan for the great encouragement he has given me by his interest in the results of this research.

*The Sir William Ramsay Laboratories*
*of Physical and Inorganic Chemistry,*
*University College,*
*London.*


## GENERAL DISCUSSION.*

**Mr. C. F. Goodeve** (*London*) said : The problem of the measurement of low osmotic pressures might be simplified by the use of a quartz spiral Bourdon gauge as first used by Bodenstein (now obtainable from Messrs. Thermal Syndicate). This instrument can be used for liquids or gases and can measure pressure differences up to 1 atmosphere. To record such a pressure, a volume change of only a fraction of a cubic millimetre is required. This would permit the rapid establishment of equilibrium. The usual sensitivity of these instruments is of the order of 1/10 mm. Hg, but by amplification methods to be described elsewhere a sensitivity up to 1/500 mm. has been obtained. The measuring of a meniscus can be completely avoided by having a tap the opening of which equalises the pressures on the two sides of the membrane. The osmotic pressure will then be given directly without correction by the difference in the gauge reading before and after the tap is closed. No advantage would be gained by filling the gauge with water unless the membrane was so rigid as not to expand under the osmotic pressure.

**Dr. G. S. Adair** (*Cambridge*) said : The osmometer devised by Mr. Oakley eliminates a source of error due to capillarity which is of great importance in the measurement of small osmotic pressures. In the earlier types of osmometer, where the colloidal solution is present in the manometer tube, it may be advisable to use tubing of 3 mm. bore, for measurements with dilute solutions, although tubing of 1·2 mm. may be suitable for experiments where the pressure exceeds 100 mm.

**Professor F. G. Donnan** (*London*) said : I doubt whether the suggestion of Mr. Goodeve is a practicable one. It would, however, be a matter of great interest to see how far the method suggested by him could be utilised in the measurement of very low osmotic pressures. The method devised by Mr. Oakley constitutes a great advance in delicate osmometric technique and has already yielded very valuable results.

**Dr. Conmar Robinson** (*London*) said : Dr. Adair has pointed out that his values for the membrane potentials of Congo Red are not in agreement with those obtained by Azuma and Kamyeama. I do not know if Dr. Adair is aware that the method of purifying the Congo Red used by the latter authors (which included salting out with $NH_4CO_3$) gave them a product which must have consisted largely of the *ammonium*

* On the two previous papers.

salt, as has already been pointed out by Robinson and Mills.[1] For this reason alone the results might be expected to be different.

Dr. Adair has given a value of − 1 for the " mean valence of the colloidal ion." This value, the " apparent " valence, is, of course, not the same as the " real " valence of the micelle, given by the number of charges it carries. Has Dr. Adair any opinion as to how large this " real " valence is in the case of Congo Red ?

**Dr. Adair** said : The question raised by Dr. Robinson cannot be answered from the data now available, but on the assumption that the proportion of free and combined sodium ions is constant, valences of 10 or more may be anticipated in solutions where the mass of the micelle of congo red is known to exceed 7000.

[1] *Proc. Roy. Soc.*, **131A**, 576, 1931.

# PART II. SPECIAL AND TECHNICAL.

## A. SOAPS AND OTHER LONG CHAIN ELECTROLYTES.

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# THE ACTIVITY OF SOAP SOLUTIONS AT 90°.

By J. W. McBain and Margaret M. Barker.

*Received 27th June*, 1934.

A misprint in the tables of Landolt-Börnstein [1] for the vapour pressure of water at 89·9°, affecting all values between 90·0° and 89·8°, distorted the calculations of Randall, McBain and White [2] for the activity of soap
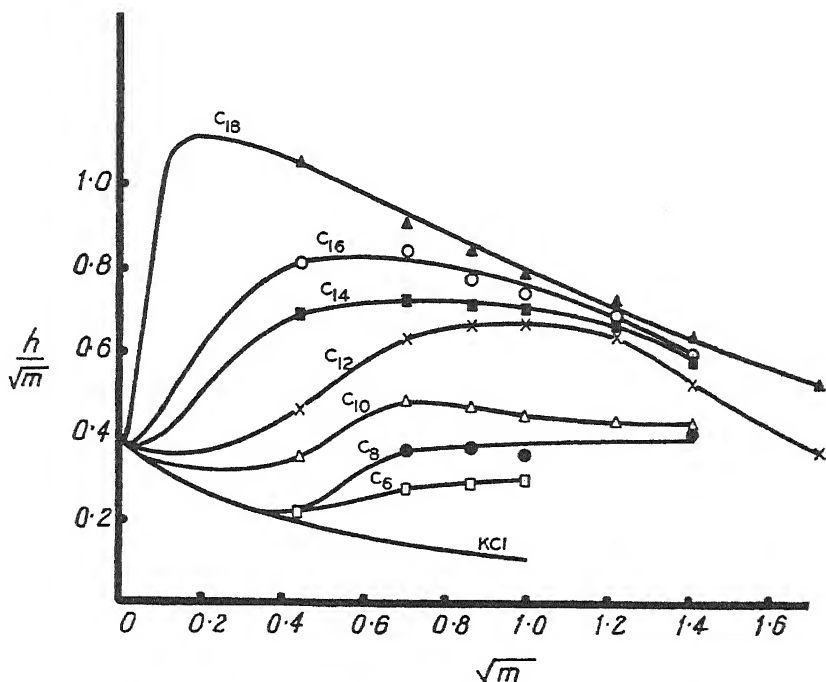


Fig. 1.—Graphs of $h/\sqrt{m}$ for potassium soap solutions at 90°.

solutions. The corrected values are recorded below, calculated by the same method.[3]

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[1] *Landolt-Börnstein physikalisch-chemische Tabellen*, Bd. 2, p. 1318, 1923.
[2] Randall, McBain and White, *J. Amer. Chem. Soc.*, **48**, 2517, 1926.
[3] Compare Randall and Allen, *J. Amer. Chem. Soc.*, **52**, 1817, 1930 ; Randall and Vietti, *J. Amer. Chem. Soc.*, **50**, 1532 1928, footnote 11 ; Hoskins, Randall and Schmidt, *J. Biol. Chem.*, 88, 215, 1930.

Fig. 1 presents the graphs for the potassium soaps and Fig. 2 those for the sodium soaps, the experimental data being those of McBain and Salmon [4] who determined the lowering of vapour pressure by dew point method at 90°.

The values of $\gamma$ are recorded in Table I. As standards of comparison are given the activity data for potassium chloride,[5] and those for an ideal binary molecule dissociating into ideal single molecules with a dissociation constant $K = 0.01$; also the activities (designated "practical" in the table) which would be found for partially dissociated electrolytes of values $K = 0.01$ and $K = 1$, if their ions are like those of potassium chloride and their undissociated part ideal. Comparison of these columns shows the effect of the lack of ideality of actual ions.
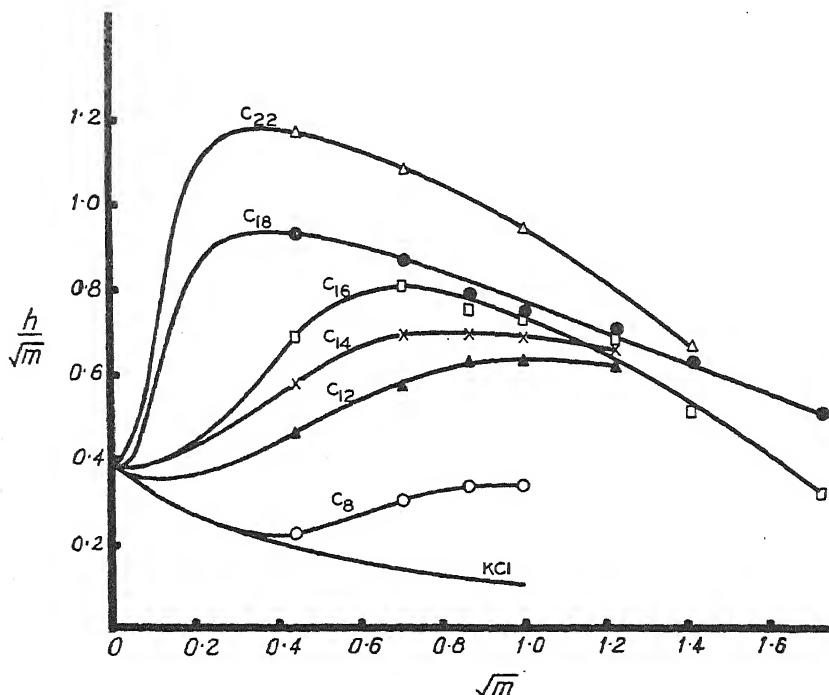


FIG. 2.—Graphs of $h/\sqrt{m}$ for sodium soap solutions at 90°.

Further, as is well known, values of $\gamma$ are nearly identical with degrees of dissociation, $\alpha$, in ideal solutions of incompletely dissociated electrolytes. The values of $\gamma$ are given to two figures upon account of inaccuracy in these derived values; even for $1.0$ $N$ potassium chloride

[4] McBain and Salmon, *J. Amer. Chem. Soc.*, **42**, 426, 1920; *Proc. Roy. Soc.*, **97A**, 49, 1920.
[5] The activity coefficient for potassium chloride deviates from the value unity for truly ideal solutions to twice the extent and in the opposite direction from that of sucrose. Thus in molal solution, $- 0.36$ as compared with $+ 0.24$, *vide* Lewis and Randall, *Thermodynamics and the Free Energy of Chemical Substances*, p. 275 (McGraw-Hill Book Co., New York, 1923). In other words (*International Critical Tables*, **4**, 259, 263, 1928), sucrose lowers the freezing-point of water by 10.9 per cent. more than $1.858°$ and potassium chloride by 12.5 per cent. less than $2 \times 1.858°$.

there is a divergence of 4 per cent. between the best values published in 1932 by Spencer,[6] 0·6126, and in 1933 by Smith,[7] 0·589.

It is evident [8] that pronounced departure from complete dissociation is marked by the characteristic " hump " in the graphs of $h/\sqrt{m}$ against $\sqrt{m}$, and that its extent goes parallel with the height of this hump.

The discussion of soap solutions is, on the one hand, simplified by the fact that formation of polyvalent ionic micelle does not increase

TABLE I.—ACTIVITY COEFFICIENTS $\gamma$ FOR SOAP IN SOLUTIONS AT 90° AND FOR POTASSIUM CHLORIDE AND PARTIALLY DISSOCIATED SOLUTES WITH DISSOCIATION CONSTANTS EQUAL TO 1·0 AND 0·01.

| Molality. | Potassium Stearate. $C_{18}$. | Potassium Palmitate. $C_{16}$. | Potassium Myristate. $C_{14}$. | Potassium Laurate. $C_{12}$. | Potassium Decoate. $C_{10}$. | |
|---|---|---|---|---|---|---|
| 0·01 | 0·80 | 0·88 | 0·89 | 0·90 | 0·90 | |
| 0·02 | 0·70 | 0·83 | 0·84 | 0·86 | 0·87 | |
| 0·05 | 0·53 | 0·70 | 0·74 | 0·78 | 0·80 | |
| 0·1 | 0·39 | 0·57 | 0·61 | 0·70 | 0·73 | |
| 0·2 | 0·26 | 0·40 | 0·46 | 0·58 | 0·64 | |
| 0·3 | 0·20 | 0·31 | 0·37 | 0·48 | 0·55 | |
| 0·4 | 0·16 | 0·25 | 0·31 | 0·40 | 0·48 | |
| 0·5 | 0·13 | 0·21 | 0·26 | 0·34 | 0·42 | |
| 0·8 | 0·08 | 0·14 | 0·17 | 0·23 | 0·33 | |
| 1·0 | 0·07 | 0·11 | 0·14 | 0·19 | 0·29 | |

| Molality. | Potassium Octoate. $C_{8}$. | Potassium Hexoate. $C_{6}$. | Sodium Behenate. $C_{22}$. | Sodium Stearate. $C_{18}$. | Sodium Palmitate. $C_{16}$. | Sodium Myristate. $C_{14}$. |
|---|---|---|---|---|---|---|
| 0·01 | 0·90 | 0·90 | 0·86 | 0·87 | 0·89 | 0·89 |
| 0·02 | 0·87 | 0·87 | 0·76 | 0·79 | 0·85 | 0·85 |
| 0·05 | 0·82 | 0·82 | 0·57 | 0·63 | 0·75 | 0·76 |
| 0·1 | 0·77 | 0·77 | 0·40 | 0·48 | 0·64 | 0·66 |
| 0·2 | 0·71 | 0·71 | 0·26 | 0·33 | 0·48 | 0·52 |
| 0·3 | 0·64 | 0·66 | 0·18 | 0·26 | 0·37 | 0·42 |
| 0·4 | 0·57 | 0·61 | 0·14 | 0·21 | 0·30 | 0·34 |
| 0·5 | 0·52 | 0·57 | 0·11 | 0·17 | 0·24 | 0·29 |
| 0·8 | 0·42 | 0·48 | 0·07 | 0·11 | 0·16 | 0·20 |
| 1·0 | 0·37 | 0·43 | 0·05 | 0·09 | 0·13 | 0·16 |

| Molality. | Sodium Laurate. $C_{12}$. | Sodium Caprylate. $C_{8}$. | Potassium Chloride. | $K = 1$. "Practical." | $K = 0·01$. "Practical." | $K = 0·01$. Ideal. |
|---|---|---|---|---|---|---|
| 0·01 | 0·90 | 0·90 | 0·903 | 0·89 | 0·60 | 0·620 |
| 0·02 | 0·86 | 0·87 | 0·874 | 0·85 | 0·49 | 0·501 |
| 0·05 | 0·78 | 0·82 | 0·822 | 0·78 | 0·35 | 0·365 |
| 0·1 | 0·70 | 0·77 | 0·772 | 0·72 | 0·26 | 0·275 |
| 0·2 | 0·58 | 0·70 | 0·715 | 0·64 | 0·20 | 0·205 |
| 0·3 | 0·48 | 0·65 | 0·693 | 0·59 | 0·16 | 0·170 |
| 0·4 | 0·41 | 0·59 | 0·667 | 0·56 | 0·14 | 0·148 |
| 0·5 | 0·36 | 0·55 | 0·651 | 0·53 | 0·13 | 0·133 |
| 0·8 | 0·25 | 0·44 | 0·617 | 0·48 | 0·10 | 0·107 |
| 1·0 | 0·20 | 0·40 | 0·601 | 0·45 | 0·09 | 0·096 |

[6] Spencer, *J. Amer. Chem. Soc.*, **54**, 4495, 4496, 1932.
[7] Smith, *J. Amer. Chem. Soc.*, **55**, 3279, 1933.
[8] Compare also Randall and Allen, *loc. cit.*[3]

ionic strength ; presumably, as was suggested by one of us, because the charges are not on one atom but are spaced far apart.[9]  Hence, the behaviour is that of a half-weak uni-univalent electrolyte.[10]  On the other hand, formation of undissociated colloid from the undissociated soap molecules largely eliminates the lowering of vapour pressure which these would normally occasion, and thereby lowers the value of the activity coefficient $\gamma$.

The highest sodium and potassium soaps exhibit in their more concentrated solutions activities which are similar to a half-strong electrolyte whose dissociation constant $K = 0.01$.  However, although the effect may be similar the cause is different, being due to disappearance of soap molecules and fatty ions to form neutral and ionic micelle, respectively.  That the low activity in these solutions is not misleading has been repeatedly demonstrated by finding that electrolytes such as KCL, HCl and NaOH dissolved in them lower the freezing-point or the vapour pressure by a slightly greater amount than they do in pure water as solvent.  In other words, the presence of fatty ions and ionic micelle does not greatly affect and certainly does not diminish the activity of other ordinary ions.

In more dilute solutions, where colloid has disappeared, the activities are still low enough to show that these electrolytes are definitely not as strong as potassium chloride although much stronger than would correspond to $K = 0.01$.

The last three columns of Table I. of Randall, McBain and White [2] stand unaffected, referring to soaps at 0°.  At this low temperature, in concentrated solution, the activities of the higher soaps are several times smaller than at 90°, and colloid persists into greater dilutions.

Finally, since activity is so indirectly connected with the observable properties of a solution, its calculation involving the properties not merely of the solution itself but of all its dilutions down to zero concentration, it is not the most suitable criterion for examining such solutions as those of soaps whose whole character changes in different ranges of dilution.  It is much more illuminating for concentrated solutions to make comparison with those properties of dissolved substances which are thermodynamically related to the behaviour of gases and to recall that in these solutions the lowering of freezing-point and of vapour pressure is that which is attributable almost solely to the sodium or potassium ions alone.

## Summary.

The activities of sodium and potassium soaps have been calculated.  For the higher soaps in concentrated solution they simulate those of a half-weak electrolyte with dissociation constant $K = 0.01$, but the effect is due to formation of colloid.  However, in more dilute solutions, soaps are shown to be only moderately strong electrolytes.

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    *California.*

[9] This accords with a suggestion made in 1923 by Bjerrum and later corroborated by Scatchard and Kirkwood, *Physik. Z.*, **33**, 297, 1932.
  [10] J. W. McBain, *J. Amer. Chem. Soc.*, **50**, 1636. 1928.

# THE RELATION OF ELECTROKINETIC AND ELECTROLYTIC MOVEMENT, AS ILLUSTRATED BY THE TRANSPORT OF ELECTRICITY THROUGH SOAP CURDS.

By M. E. Laing McBain.

It has been shown (1924) [1] that in an electrical field the electrokinetic behaviour of sols, jellies and curds of soap may be dealt with experimentally in exactly the same manner as the electrolytic migration of ordinary ions. Indeed, it became evident that there was no essential difference between the two groups of phenomena, which are usually treated separately, and that both electrokinetics and electrolytic migration are parts of the same field of general electrochemistry. This was strikingly borne out by the experimental result that the relative movement between soap and water, and indeed the movement of each of the constituents of the soap solution, is quite independent of whether the experiment is performed as one of electrosmosis or of cataphoresis or of electrolytic migration. The essential difference between ions and colloids and other surfaces was seen to be that in ions there is one charge per chemical equivalent, whereas with most surfaces there are but few charges to many chemical equivalents. Even this distinction disappears when a colloidal particle is fully charged as in the ionic micelle of a colloidal electrolyte where there is one charge for each chemical equivalent in the particle. On the other hand, a suspension or an ordinary colloid behaves merely like a colloidal electrolyte, or indeed an electrolyte, of less charge.

It has been shown elsewhere [2] that the properties of ions may be described in terms of the hypothetical or arbitrary $\zeta$-potential used in the classical and more recent formulæ for electrokinetics, or that alternatively and preferably, the whole of the phenomena of electrokinetics may be formulated in terms of the directly observed quantities. The parallel formulæ together with further relations which still await experimental test were placed on record, the characteristic quantity being the observed movement in an electrical field.

Every constituent of the soap system was found to be in relative movement, every ion displaying its ordinary migration velocity relative to the water. These experiments, like those here described, thus definitely disprove the classical assumption of Helmholtz and a long succession of other authors that " the bulk of a liquid is carried along as it were by its skin," the description employed in discussing a capillary tube ; or, in other words, that the liquid moves at the same rate as the mobile ions of the double layer.

The present communication extends the experimental study to curds of less soluble soaps with special attention to such as contain added salt which helps to define or identify or serve as a standard of com-

[1] Laing, *J. Physic. Chem.*, **28,** 673, 1924. The following erratum should be noted : Page 682, title to Table II., 0·0145 should be 0·5145.
[2] J. W. McBain and M. E. L. McBain, *Z. physik. Chem.*, **161A,** 279, 1932 ; see also DuBois, *Z. Elektrochem.*, **38,** 764, 1932.

parison for the electrochemical properties of the system. The ultra-microscopic crystalline fibres of sodium palmitate curds at room temperature are nearly insoluble, especially in concentrated solutions of salts. The curd fibres and chlorine ions migrate independently. It is of especial interest that electrokinetic phenomena persist in these systems up to very high concentrations of salt; and they make excellent systems for demonstrating electrosmosis, even in the presence of normal solution of salt.

### Experimental Method.

The soaps were especially made for us by Kahlbaum, and the salts were Kahlbaum's "for analysis." The special analytical methods, using sodium hydroxide prepared from sodium drippings and using freshly boiled-out, carbon dioxide-free solvents throughout, have already been described. Chloride was determined gravimetrically as silver chloride. All equipment was calibrated. The analysis of the original soaps gave the following gross compositions: sodium palmitate, 0·6 equivalents per cent. excess palmitic acid, 2·4 per cent. water; sodium laurate, 1·03 equivalents per cent. excess lauric acid, 0·8 per cent. water; potassium laurate, 0·07 equivalents per cent. excess lauric acid and 0·23 per cent. water. Details of the apparatus used for migration measurements were given in reference (1). It consists of U tubes with a central portion which may be cut out with a razor butt blade through ground butt joints, the curd being contained between electrode guard solutions of sodium sulphate. Two silver coulometers were used, one at each end. Analysis was made gravimetrically for chloride, and the solution was split by a known quantity of sulphuric acid. The fatty acid and the change in titration value of the sulphuric acid (termed alkalinity in the tables) were determined separately. Calculations are based upon weight of water exactly as in accurate Hittorf determinations of migration. Corrections were made for hydrogen and oxygen evolved at the two platinum electrodes. Conductivities were determined with the best Leeds and Northrup equipment available, using precautions suggested by Grinnell Jones, and later with the Grinnell Jones bridge itself. Mother liquor was pressed out from a separate sample of the same or similar curd with the Carver press at 10,000-12,000 lbs. per sq. in. and duplicate analyses were made. Soap content in the absence of salt was determined with a dipping refractometer and auxiliary prism.

In a migration all glassware was first weighed dry, then the soap introduced into the middle portion and cooled to solidify as curd. Guard solutions of neutral sodium sulphate were weighed in from weighing burettes.

### Calculation of Results.

Since the chief point of this paper is that it illustrates equally the phenomena of electrokinetics and of electrolytic migration and their simultaneous treatment on either basis and since the essential identity of these two fields is not yet commonly recognised, it may be well to refer to the familiar form of diagram of transference phenomena, such as might have been employed in the classical experiments of Hittorf, to illustrate the state of affairs before and after electrolysis :—

| | | Na | Na | Na | Na | | Na | | Na | Na | Na | Na | Na | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Anode | P | P | P | P | | P | | P | P | P | P | P | Cathode |
| | | Na | Na | Na | Na | | Na | | Na | Na | Na | Na | Na | |
| | | Cl | Cl | Cl | Cl | | Cl | | Cl | Cl | Cl | Cl | Cl | |

| | | | | | Na | Na | | Na | | Na | Na | Na | Na | Na | Na | Na |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | P | P | P | P | P | | P | | P | P | P | P | | | |
| | | | | | Na | Na | | Na | | Na | Na | Na | Na | Na | Na | Na |
| Cl | Cl | Cl | Cl | Cl | Cl | Cl | | Cl | | Cl | Cl | | | | | |

The solutions are separated from the electrodes by the guard solutions of sodium sulphate, thus leaving the part of the system in which we are interested unaffected by unknown electrode reactions.

Study of the diagram shows that the soap conducts current in proportion to the fraction which its conductivity bears to the total conductivity of the system. This is true whether the soap is in solution, or exhibiting surface conductivity out of solution, or both. There is no conceivable way in which soap may be moved by the current without such shear of positive and negative carriers and the corresponding amount of electrolysis. The only cations present in these faintly alkaline solutions ($p_H$ 8-9) are sodium ions, and the statements just made hold good for any form or forms in which soap may be present, whether it is fully dissociated into simple sodium and fatty ions or into ionic micelles and fatty ions or insoluble negatively charged curd fibres with their corresponding mobile sodium ions. Thus the essential validity of such diagrams is not affected by loading each fatty ion, represented by the symbol P, with any amount of neutral soap.

It is also seen from the diagram that the transport numbers of fatty radical, 0·125, and of chloride, 0·375, are given by the proportion of their movement (1 and 3, respectively) to the total coulometer reading (8). The diagram is, of course, arbitrary and the actual movements are given by experiments in the tables.

Consideration of the " alkalinity " titration, that is, titration of the standard sulphuric acid with which the soap is split in analysis, shows that after subtracting the number of equivalents equal to the total coulometer at the cathode and adding the same quantity at the anode, the change at both electrodes is identical with that measured by the change in concentration of the fatty acid. Hence, each experiment yields four independent values for the movement of fatty radical. Had the soap been appreciably alkaline there would have been a slight discrepancy between the change in alkalinity and the change in fatty radical which would give the part of the coulometer reading due to the current carried by free sodium hydroxide. This was negligible in all the experiments here considered.

Analyses were based upon weight of solvent. At the cathode chlorine found after electrolysis was taken as sodium chloride, alkalinity as free sodium, fatty radical as anhydrous fatty radical, the coulometer equivalent as free hydrogen, the balance being water. Likewise, at the anode fatty radical is taken as such, alkalinity plus coulometer equivalent as sodium, total coulometer as chlorine, sodium chloride minus total coulometer equivalents as sodium chloride, total coulometer as oxygen, the balance being water. In cases where the equivalents of sodium chloride obtained in analysis were less than the total coulometer reading, the deficit was subtracted from the sodium.

### The Experimental Data.

Electrolysis had to be stopped when through electrosmosis the liquid left the anode bare or filled the free space in the cathode compartment. The plug of soap did not move, there was no convection, and in no case was sulphate found in the middle portion.

Table I. records the compositions of the systems studied, together with the results obtained for migration. In addition, in many cases the specific conductivity of the system was measured, and where possible the composition of liquid expressed from the curd by pressure was determined. All concentrations are expressed in weight normality, $N_w$ ; that is, molality.

Probably the chief factor in causing divergences between duplicate experiments lies in the incomplete establishment of equilibrium when the curd is solidified by cooling the hot solution within the apparatus. This

TABLE I.—MIGRATION DATA IN CURDS OF SODIUM LAURATE OR SODIUM PALMITATE, WITH AND WITHOUT SODIUM CHLORIDE OR POTASSIUM CHLORIDE. A = ANODE, M = MIDDLE, C = CATHODE.

| System $N_w$. | Temperature. | Coulometer Equivalents. | Migration. | | |
|---|---|---|---|---|---|
| | | | Alkalinity. | P or L. | Cl. |
| 1 NaP + 0·5 NaCl . | 20–22° | 0·002841 | A +0·603 | +0·578 | +0·560 |
| | | 110 volts | M +0·01 | −0·04 | −0·01 |
| | | 120 minutes | C −0·636 | −0·688 | −0·555 |
| 1 NaP + 0·5 NaCl . | 20–22° | 0·001698 | A +0·606 | +0·648 | +0·560 |
| | | 110 volts | M | none—spilled | |
| | | 90 minutes | C −0·481 | −0·556 | −0·564 |
| 1 NaP + 0·5 NaCl . | 13–19° | 0·002984 | A +0·741 | +0·737 | +0·629 |
| | | 150–300 volts | M −0·05 | +0·06 | −0·03 |
| | | 120 minutes | C −0·439 | −0·788 | −0·656 |
| 1 NaP + 0·1 NaCl . | 20° | 0·001654 | A +2·42 | +2·44 | +0·455 |
| | | 110 volts | M +0·08 | +0·04 | −0·04 |
| | | 120 minutes | C −2·45 | −2·37 | −0·410 |
| 1 NaP + 0·1 NaCl . | 19° | 0·001700 | A +1·665 | +1·605 | +0·385 |
| | | 110 volts | M +0·003 | −0·001 | +0·009 |
| | | 120 minutes | C −1·659 | −1·609 | −0·357 |
| 1 NaP + 0·1 NaCl . | 20° | 0·000683 | A +5·51 | +5·44 | +0·390 |
| | | 110 volts | M −0·14 | −0·12 | −0·21 |
| | | 73 minutes | C −5·05 | −4·81 | −0·460 |
| 1 NaP . . . | 18° | 0·000818 | A +7·25 | +7·11 | — |
| | | 110 volts | M +0·01 | +0·01 | — |
| | | 90 minutes | C −7·20 | −7·07 | — |
| 1 NaP . . . | 17° | 0·000547 | A +9·51 | +9·97 | — |
| | | 250 volts | M −0·07 | — | |
| | | 55 minutes | C −9·97 | −9·82 | |
| 1 NaP + 1 KCl . | 16° | 0·001861 | A +0·312 | +0·377 | +0·580 |
| | | 500 volts | M −0·001 | −0·001 | +0·002 |
| | | 100 minutes | C −0·361 | −0·332 | −0·493 |
| 1 NaL + 1 KCl . | 16–19° | 0·002131 | | | |
| | | 500 volts | | | |
| | | 120 minutes | C −0·243 | −0·253 | −0·413 |
| 1 NaL + 1 KCl . | 12° | 0·002385 | A +0·309 | +0·347 | +0·537 |
| | | 110 volts | M −0·024 | −0·004 | −0·034 |
| | | 80 minutes | C −0·338 | −0·343 | −0·483 |
| 0·5 NaL + 1 KCl . | 9° | 0·001424 | A +0·178 | +0·255 | +0·604 |
| | | 500 volts | M +0·03 | +0·04 | +0·02 |
| | | 80 minutes | C −0·147 | −0·133 | −0·436 |
| 1 NaL + 1 NaCl . | 14–20° | 0·001857 | A +0·092 | +0·182 | +0·530 |
| | | 500 volts | M −0·029 | +0·045 | +0·009 |
| | | 100 minutes | C −0·210 | −0·176 | −0·607 |
| 1 NaL + 1 NaCl . | 10–14° | 0·003548 | A +0·194 | +0·257 | +0·668 |
| | | 500 volts | M −0·045 | +0·023 | +0·009 |
| | | 165 minutes | C −0·151 | −0·181 | −0·667 |
| 1 NaL + 0·5 NaCl . | 18° | 0·001817 | A +0·413 | +0·381 | +0·639 |
| | | 110 volts | M +0·035 | +0·029 | +0·001 |
| | | 120 minutes | C −0·392 | −0·339 | −0·628 |
| 1 NaL + 0·5 NaCl . | 18–20° | 0·003731 | A +0·277 | +0·292 | +0·649 |
| | | 110 volts | M −0·012 | −0·010 | −0·029 |
| | | 180 minutes | C −0·275 | −0·281 | −0·662 |
| 1 NaL + 0·5 NaCl . | 20–21° | 0·002800 | A +0·655 | +0·665 | +0·600 |
| | | 110 volts | M +0·025 | +0·013 | +0·015 |
| | | 120 minutes | C −0·524 | −0·532 | −0·605 |
| 1 NaL + 0·1 NaCl . | 19–20° | 0·001764 | A +1·20 | +1·23 | +0·34 |
| | | 110 volts | M −0·05 | −0·03 | −0·01 |
| | | 110 volts | C −1·29 | −1·31 | −0·30 |
| 1 NaL + 0·1 NaCl . | 20° | 0·001539 | A +1·74 | +1·69 | +0·390 |
| | | 110 volts | M +0·06 | +0·24 | +0·00 |
| | | 100 minutes | C −1·76 | −1·48 | −0·326 |
| 1 NaL + 0·1 NaCl . | 22° | 0·001805 | A +1·24 | +1·36 | +0·295 |
| | | 110 volts | M −0·04 | −0·04 | −0·04 |
| | | 120 minutes | C −1·19 | −1·21 | −0·268 |
| 1 NaL . . . | 18° | 0·001174 | A +5·12 | +5·26 | — |
| | | 110 volts | M −0·02 | −0·10 | — |
| | | 110 minutes | C −5·36 | −5·36 | — |
| 0·5 NaP + 0·5 Na Oleate . | 14–16° | 0·001096 | A +2·07 | +1·98 | — |
| | | 250 volts | — | — | — |
| | | 80 minutes | C −2·01 | −2·00 | |

is partly mechanical, curd fibres grouping themselves differently, and also partly due to differences in hydration of the curd at different temperatures and concentrations as has been described elsewhere.

Two experiments were done with 1 $N$ sodium palmitate in 5 per cent. aqueous glycerine. The mean of the eight closely agreeing results for transference for soap radical is 6·73, distinctly less that that in pure water. The glycerine analyses were insufficiently accurate in the presence of so much soap but would indicate, if they could be trusted, a slight positive sorption of glycerine by the soap which, however, is not in accord with other previous direct measurements.

### The Summarised Data.

The results are summarised in Table II. The mixture 1 NaP + 1 NaCl proved to be impossible of study since it could not be made homogeneous at any temperature as it falls in the heterogeneous portion of the phase rule diagram.[3]

TABLE II.—MIGRATIONS OBSERVED IN CURDED SYSTEMS, SHOWING PRO- PORTION OF CURRENT CARRIED BY SALT (NaCl coul.) AND SOAP (soap coul.) ; ALSO THE SPECIFIC CONDUCTIVITY, $\kappa$, OF THE SYSTEM.

| System. | $n$. P or L. | $n_{Cl}$. | NaCl Coul. | Soap Coul. | $\kappa$†. |
|---|---|---|---|---|---|
| 1 NaP + 0·5 NaCl . . | 0·647 | 0·572 | 0·89 | 0·11 | 0·02225 |
| 1 NaP + 0·1 NaCl . . | 3·09 | 0·410 | 0·57 | 0·43 | 0·00640 |
| 1 NaP . . . | 8·24 | — | 0 | 1·00 | 0·00265 |
| 1 NaP + 1 KCl . . | 0·313 | 0·495 | 0·96 | 0·04 | 0·0402 |
| 1 NaL + 1 KCl . . | 0·334 | 0·510 | 0·97 | 0·03 | 0·06902 |
| 0·5 NaL * + 1 KCl . . | 0·194 | 0·52 | 1·00 | 0 | 0·08401 |
| 1 NaL + 1 NaCl . . | 0·180 | 0·616 | 0·95 | 0·05 | 0·0516 |
| 1 NaL + 0·5 NaCl . . | 0·415 | 0·631 | 0·97 | 0·03 | 0·02405 |
| 1 NaL + 0·1 NaCl . . | 1·39 | 0·320 | 0·53 | 0·47 | 0·0100 |
| 1 NaL . . . | 5·28 | — | 0 | 1·00 | 0·00427 |
| 0·5 NaP + 0·5 Na Oleate . | 2·01 | — | 0 | 1·00 | — |

\* $\kappa_{18°} = 0·00303$.

† It should be remembered that, since results are expressed in molality or weight normality $N_w$ and soaps are so bulky, the equivalent conductance of 1 $N_w$ sodium palmitate, for example, is obtained by multiplying $\kappa$ by approximately 1278 instead of the 1000 used for volume normality.

The soap content of the mother liquor of sodium palmitate containing 0·5 NaCl, 0·1 NaCl, and 1 KCl was 0·022 $N$, 0·021 $N$, and 0·015 $N$, respectively, by refractive index. That for 1 NaL with 1 KCl, 0·5 NaCl, and alone was 0·20 $N$, 0·021 $N$, and 0·237 $N$, respectively, by refractive index. That for 0·5 NaL with 1 KCl was 0·13$N$. Direct analysis showed that the mother liquor from 1 NaP was 0·021 N. and that 1 NaL with 0·5 NaCl contained 0·017 equivalent of soap and 0·525 equivalent of chloride, that 1 NaL + 0·1 NaCl contained 0·125 equivalent of soap and 0·138 equivalent of chloride.

### Discussion.

**Electrokinetic Movement Prominent.**—The first thing to note is that in all cases there is a large movement of soap even when none of it is in solution and even in concentrated salt solution. The largest value in the second column is 8·24 equivalents of soap moved for each

[3] For references, see McBain, Lazarus and Pitter, Z. physik. Chem., **147**A, 87, 1930.

faraday of current for normal sodium palmitate of which the specific conductivity is low and only about $2 \cdot 1$ per cent. is in solution ($0 \cdot 021$ $N$ at $20°$). Laurate is very much more soluble than palmitate, the dissolved portion being $0 \cdot 25$ $N_w$ in the absence of salt and mostly colloidal electrolyte.

**An Appreciable Fraction of the Current carried by Electrosmosis.** —The next feature is the relation which the motion of the chloride ion bears to the value which it would possess for sodium chloride alone, $0 \cdot 610$, $0 \cdot 626$, and $0 \cdot 635$ for $0 \cdot 1$, $0 \cdot 5$, and $1 \cdot 0$ $N$ sodium chloride, respectively.[4] Where this value is equalled or slightly exceeded in the third column of the table, it is proof that nearly the whole of the current is carried by the sodium chloride. Where only soap is present the soap coulometer becomes 1.

Where the transport of the chlorine is very low it clearly follows that only a part of the current is borne by the salt, the balance being carried by the soap. Here the conductivity of the soap, whether surface or bulk or both, becomes comparable with that of the salt. A striking case is afforded by the second line of Table II., for 1 NaP + $0 \cdot 1$ NaCl. Here almost all the soap is out of solution as curd fibres, a fact clearly demonstrated by the low concentration of soap ($0 \cdot 021$ $N$) in the expressed mother liquor. Yet the salt carries less than three-fifths of the current. The balance is therefore surface conductivity of the soap, accounting for over two-fifths of the total coulometer, and equalling two-thirds of the conductivity of decinormal sodium chloride, and accounting for the observed movement of $3 \cdot 09$ equivalents of soap for 1 faraday of total current or $0 \cdot 43$ faradays of current carried by itself. The migration number of the sodium of the soap is $0 \cdot 43 - 3 \cdot 09 = - 2 \cdot 66$; that of the sodium of the sodium chloride in solution is $0 \cdot 57 \times 0 \cdot 610$ $= + 0 \cdot 35$. For the current carried by the soap the migration number of the fatty radical in its electrokinetic movement or electrosmosis must be $3 \cdot 09 / 0 \cdot 43 = 7 \cdot 2$ equivalents per faraday, and that of the sodium $1 - 7 \cdot 2 = - 6 \cdot 2$ equivalents per faraday. Within the experimental error this is the same as the observed result in the next line, $8 \cdot 2$, for sodium palmitate curd with no salt, and also that observed in the first line ($0 \cdot 647$) when referred to the fraction of the current carried by the soap curd; namely, $0 \cdot 647 / 0 \cdot 07 = 9 \cdot 2$.

One can therefore by inspection approximately predict the result for the last line of Table II., a mixture containing $0 \cdot 5$ NaP + $0 \cdot 5$ Na Oleate. The latter constituent alone has a conductivity about equal to that of $0 \cdot 1$ $N$ sodium chloride. Hence, by comparison with line 2 of Table II. the sodium palmitate would yield a migration of about $1 \cdot 5$ for the contribution of the $0 \cdot 5$ $N$ palmitate. The migration of the oleate is $1 \cdot 0$, but carrying only two-thirds of the current reduces its contribution to $0 \cdot 6$, giving a total of $2 \cdot 1$ as compared with the observed value, $2 \cdot 0$. Closer calculation is not possible, as it has been shown previously that some interaction occurs between these two constituents.

This assumption of a constant surface conductivity for palmitate fibres serves as a first approximation. It may be recalled that in the previous communication (1924) it was found that a similar ascription of constant conductance or migration value to undissociated sodium oleate, whether in solution or as curd fibres, served to account for the observed data with all concentrations of oleate sols, jellies, and curds.

[4] *International Critical Tables,* **6**, 310, 1929; also $0 \cdot 510$ for $1N$ potassium chloride at $18°$.

It was only necessary to take definite values of the migration number of simple fatty ion, ionic micelle and undissociated colloid, respectively, to account quantitatively for all observations.

**Mechanical Obstruction caused by Curd Fibres.**—Insoluble curd fibres play two rôles. They serve as a source of surface conductance and also as a mechanical obstruction to the passage of current. They are self ionising and not like glass dependent upon carriers brought in from outside. It is interesting to see how far calculation of the palmitate curds can go in continuation of these first simple approximations. The specific conductivity given in the second line of Table II. for the curd containing $0.1$ NaCl is $0.00640$, whereas that for the chloride alone would have been $0.00918$, and from the way in which current is shared between surface conductance of curd and chloride, according to the coulometer readings (which automatically reveal the relative conductivities of the constituents) this should be increased in the proportion $1/0.57$, giving $0.0161$ for the total conductivity of the mixture. Hence the obstruction (and some sorption of chloride) has reduced this value by 60 per cent.

In the absence of salt (line 3 of Table II.) one might look for the same surface conductivity; namely, $0.0069$ plus the specific conductivity of the simple crystalloidal mother liquor which is $0.02$ $N_w$ sodium palmitate half dissociated, and therefore should have a specific conductivity $0.00057$. The total specific conductivity predicted is the sum of the two items mentioned; that is, $0.0074$ which, when compared with $0.00265$ found, indicates an obstruction of 65 per cent.

In similar fashion, one predicts for the first line in Table II. that the sum of this surface conductivity and the known specific conductivity of $0.5$ $N$ sodium chloride would be $0.0472$ which, compared with that observed, $0.02225$, gives the obstruction 53 per cent.

Incidentally, the fact that the obstruction to passage of the current by the presence of curd fibres doubles the resistance is highly significant when one remembers that the formation of a clear jelly does not appreciably affect conductivity. Curd fibres are soap that has crystallised out from solution; jellies are formed by linkage of existing particles.

**Absolute Mobilities and " $\zeta$-Potentials."**—There are two interesting methods of calculating the linear mobility and $\zeta$-potential of each of the constituents from fundamental general principles. The first and simplest is to deduce from the observed migration of a constituent and the specific conductivity the linear movement which would have occurred for 1 volt per centimeter.

Thus for palmitate in the system 1 NaP + $0.1$ NaCl in line 2 of Table II., the migration recorded is $3.09$ equivalents per faraday. Since the solution is normal with respect to palmitate, this would be contained in 3090 c.c., and this amount must pass through any cross-section and any part of it must traverse a path 3090 cm. long whenever 1 faraday of current passes through the total system of 1 sq. cm. cross-section. The time in seconds required to pass this total current of 96500 coulombs with an E.M.F. of 1 volt per cm. is 96500 divided by the specific conductivity actually observed. Hence $u$ of curd fibres in line 2 becomes $3090 \times 0.00640/96500 = 20.5 \times 10^{-5}$ cm./sec./volt./cm. Similarly, for the chlorine ion $u = 27.2 \times 10^{-5}$ cm./sec./volt./cm.

For comparison it should be recalled that all such data in electrochemical literature have been derived by combination of the total conductivities of the actual solution, which gives the sum of the

mobilities of all ions present (and for single salts is equal to the conductivity at infinite dilution multiplied by the Arrhenius conductivity ratio $\alpha$), with the migration number of the salt in that actual system or concentration, which gives the portion of the current carried by the ion in question. For example, from standard data for a decinormal solution of pure sodium chloride at 18°, the mobility of the chlorine ion $= 91\cdot82 \times 0\cdot610/96500 = 58\cdot0 \times 10^{-5}$ cm./sec./volt/cm.

**Obstructed and Unobstructed Mobility.**—Not this value, but $27\cdot2$ is given by applying this calculation to line 2 of Table II., column 3. This is because of the obstruction in our present system caused by the curd fibres. The ratio of observed to expected mobility is 47 per cent. There are thus two mobilities of interest, the practical value in the actual obstructed system where the cross-section is reduced and the path of the current lengthened and a higher voltage is required to produce the current or movement, and the free mobility such as would obtain without obstacles as, for example, for a single fibre suspended in the fluid medium.

$\zeta$-potentials have never been observed in any system and may have little bearing upon the potentials actually present in the system. They are always deduced by calculation, in process of which $u$ is multiplied by $\frac{4\pi\eta}{D}$ according to the Helmholtz-Smoluchowski derivations (or $\frac{6\pi\eta}{D}$ in certain cases, applying the Debye-Hückel factor). At 18° this factor is $14\cdot84 \times 10^4$. Thus for chlorine ion at infinite dilution $\zeta = 96\cdot8$ millivolts which in $0\cdot1$ $N$ sodium chloride falls to the value of $84\cdot7$ millivolts. They thus derive their sole significance from the magnitude and sign of the experimental [5] observable quantity $u$. The values for the $u$'s or $\zeta$'s in our systems are collected in Table III.

**Standard and Idealised Mobilities.**—The second method of calculating $u$ for our mixed migrations is to compare the actual movement of fatty radical with that exhibited by any other known ion in the same system and necessarily subject to the same conditions, arriving at the value for $u$ by simple proportion with the known value for the standard ion. Thus in line 2 of Table II. for the system 1 NaP $+$ 0·1 NaCl comparison may be made between the actual movements of fatty radical and chlorine ion and the standard known value for chlorine ion in ordinary decinormal sodium chloride, $58\cdot0 \times 10^{-5}$. The ratio of the observed movements has to be corrected for the respective concentrations. Hence, for curd fibres for unobstructed movement

$$u = \frac{3\cdot09}{0\cdot410} \times \frac{0\cdot1}{1} \times 58\cdot0 \times 10^{-5} = 43\cdot7 \times 10^{-5} \text{ cm./sec./volt/cm.}$$

and $\zeta$ would be 64·9 millivolts. For an obstruction of 53 per cent. these would become $20\cdot5 \times 10^{-5}$ and 30·4 millivolts, respectively (compare the values in columns 2 and 3 of Table III. below).

The calculation for line 3 of Table II., sodium palmitate only, is not quite so simple because the reference substance upon which to base the comparison here is simple fatty ion itself, which as a heavy organic ion should have a mobility of 20 mhos. The concentration actually in solution is only 0·021 $N$, half dissociated, with sufficient hydrolysis

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[5] The conventional method of observation is to observe the linear velocity which could have been done in the present measurements but would have required auxiliary electrodes in the end to determine the potential gradient operative at the boundary.

alkali to conduct an almost equal amount of current. However, most of the current is due to surface conductivity of the insoluble curd fibres already evaluated. This leads directly to the values given in Table III., columns 6 and 7.

TABLE III.—LINEAR MOBILITIES AT 18° IN CM. /SEC. /VOLT/CM. × 10⁵ FOR FREE MOVEMENT AND FOR ACTUAL OBSTRUCTED MOVEMENT, AND ζ-POTENTIALS (IN MILLIVOLTS) OF THE CONSTITUENTS PRESENT.

| System. | Actual * (Obstructed). | | | | Idealised (Unobstructed). | | | |
|---|---|---|---|---|---|---|---|---|
| | $u_{soap}$ | $\varsigma_{soap}$ | $u_{Cl}$ | $\varsigma_{Cl}$ | $u_{soap}$ | $\varsigma_{soap}$ | $u_{Cl}$† | $\varsigma_{Cl}$ |
| 0.5 NaCl | — | — | 52.4‡ | 77.8‡ | — | — | 52.4 | 77.8 |
| 1 NaP + 0.5 NaCl . | 14.9 | 22.1 | 26.4 | 39.2 | 29.6 | 44.0 | 52.4 | 77.8 |
| 1 NaP + 0.1 NaCl . | 20.5 | 30.4 | 27.2 | 40.3 | 43.7 | 64.9 | 58.0 | 86.1 |
| 1 NaP . . | 21 | 31 | — | — | 67 | 99 | — | — |
| 1 NaP + 1 KCl . | 13.0 | 19.4 | 20.6 | 30.6 | 32.8 | 48.7 | 51.8 | 76.9 |
| 1 NaL + 1 KCl . | 23.9 | 35.5 | 36.5 | 54.2 | 34.0 | 50.4 | 51.8 | 76.9 |
| 0.5 NaL + 1 KCl . | 33.8 | 50.1 | 45.3 | 67.2 | 38.7 | 57.4 | 51.8 | 76.9 |
| 1 NaL + 1 NaCl . | 9.6 | 14.3 | 32.9 | 48.9 | 14.3 | 21.2 | 48.8 | 72.4 |
| 1 NaL + 0.5 NaCl . | 10.3 | 15.3 | 31.5 | 46.7 | 16.6 | 24.7 | 52.4 | 77.8 |
| 1 NaL + 0.1 NaCl . | 14.4 | 21.4 | 33.2 | 49.2 | 25.2 | 37.4 | 58.0 | 86.1 |
| 1 NaL . . | 23.4 | 34.7 | — | — | 48 | 71 | — | — |

\* From observed migration and observed specific conductivity.
† From data of *International Critical Tables*.

**Sorption of Chloride by Curd Fibres.**—Although sodium chloride solutions becomes more concentrated when placed in contact with anhydrous soap fibres, owing to the water of hydration which they abstract, nevertheless sodium chloride is positively adsorbed by the fibres, as shown by Salmon's measurements,[6] to the extent of 0.3 per cent. by weight in dilute solution up to several per cent. in saturated salt solution. Hence, in the present experiments this must be a distinct although minor factor. Any undissociated sodium chloride or chlorine ions adsorbed must move at the same rate as the soap and this movement will be additional to that due to electrolysis of the free electrolyte. Its presence becomes clearly demonstrated where the total movement of chlorine, as exhibited in column 3 of Table II. is increased beyond the highest value which could be produced by the free ions of sodium chloride alone. We have in every case in Table II. arbitrarily allowed for 0.4 per cent. by weight of chlorine (or 2 mols. per cent.) on palmitate fibres and 5 mols. per cent. on laurate fibres.

As regards sorbed chloride, its movement is that of the curd fibres regardless of whether only chlorine ions or sodium chloride molecules or both are sorbed.

**The Mobilities and ζ-Potentials in Table III.**—The mobilities deduced for soap in Table III. are mean values for all the forms of soap present in the particular system. In most cases these are chiefly curd fibres, but for laurate alone or in admixture with potassium chloride the solubility is appreciable. Similarly, a minor correction might have been made in the actual mobility of chloride to allow for the small

[6] McBain and Salmon, *J. Chem. Soc.*, **119**, 1374, 1921.

proportion of the chloride which is sorbed on moving fibres and colloidal soap. The $\zeta$-potentials have been calculated from the corresponding $u$ values by multiplying by the factor $14\cdot84 \times 10^4$. In other words, they have not been corrected for any influence which the dissolved substances have upon viscosity. This merely follows the usual convention in calculating $\zeta$-potentials that a viscosity exactly equal to that of water is exhibited unaltered, no matter how thin the layer or short the distance between charges and surfaces.

Comparison between corresponding values and the right- and left-hand portions of the table yields approximately the obstructional effect of the undissolved soap in diminishing the effect of cross-section of the conducting system. It is, as expected, greater for insoluble palmitate fibres than for the more soluble laurate. Likewise the $u$ and $\zeta$ values are less for laurate than for palmitate.

Considering any one series, the most striking feature is, of course, the persistence of appreciable mobility and therefore " $\zeta$-potentials " even in presence of strong salt solutions. It may be recalled that a similar finding was made in this laboratory in the study of surface conductivity of glass surfaces in contact with strong solutions of salts.[7]

A certain amount of metathesis occurs when sodium soaps are mixed with potassium chloride, especially since all our soaps are originally made homogeneous by being heated to complete liquefaction before they are allowed to solidify in the apparatus. The solubilities and the other values are thereby distinctly increased. The palmitate is, of course, least affected.

**Origin of the Charge on Curd Fibres.**—The foregoing discussion and the observed migration values in Table II. show conclusively that, although some of the charges on curd fibres may possibly be derived from unpaired adsorption of chloride ions, most of the charges on the curd fibres are due to surface dissociation of the fibres themselves. The concentration of free hydrolysis alkali is negligible in these experiments, and from previously published data on the slight sorption of sodium hydroxide by soap fibres it is evident that sorbed hydroxyl ions are too few to be of significance. The movement of chloride and fatty radical is measured separately as shown in Table II., and the slight amount of chloride attached to the moving fibres is far too small to account for their movement and their large conductivity.

**Magnitude of the Charge upon Curd Fibres.**—The following simple calculation, based upon the now familiar equations of the previous paper, gives numerical values for the number and mobilities of the charges present in the so-called double layer of the curd fibres. It shows that the sodium ions which actually move possess almost the same mobility as ordinary sodium ions of $N/10$ solution, and that their concentration is approximately $0\cdot07$ $N$ Na$^\bullet$. The calculation is for line 2 of Table II., $1$ NaP $+ 0\cdot1$ NaCl, an especially favourable case for study because the current is shared almost equally between the soap (43 per cent.) and the sodium chloride (57 per cent.).

The conductivity of the amount of system containing 1000 g. of water, or about 1278 c.c., $\mu = 1278 \times 0\cdot00640 = 8\cdot18$ mhos. The migration of the soap observed was $3\cdot09$, but correcting for the contribution of dissolved soap this becomes $3\cdot03$. Hence the migration

[7] McBain, Peaker and King, *J. Amer. Chem. Soc.*, **51**, 3294, 1929 ; see also McBain and Foster, *Colloid Symposium Monograph*, **11**, 1934 ; *J. Physic. Chem.*

number of the curd fibres $n_1 = 3\cdot03 = \dfrac{c_1 m_1 f_1}{\mu} = \dfrac{m_1 f_1}{8\cdot18}$, where $c_1$ is 1 $N$.
Hence $m_1 f_1 = 24\cdot79$ and $f_1 = 24\cdot79/m_1$, where $f_1$ is the mobility of the negative charge on the curd fibres and $m_1$ is the number of chemical equivalents carrying 1 faraday of such charge.

The specific conductivity due to total soap is $0\cdot43 \times 0\cdot00640 = 0\cdot00275$, and therefore for 1000 g. water $1278 \times 0\cdot00275 = 3\cdot51$ mhos. The small part of the soap in solution, had it been alone, would have had a specific conductance of $0\cdot00057$ or for 1278 c.c. $0\cdot73$ mho. Now from the right- and left-hand halves of Table III., it appeared that the obstruction amounted to $53\cdot1$ per cent. which would reduce this to $0\cdot73 \times 0\cdot469 = 0\cdot35$ mho, leaving $3\cdot16$ mhos as the conductivity of the $0\cdot98$ $N_w$ undissolved curd fibres. This $3\cdot16$ mhos is obviously the sum of the negative and positive carriers and the latter can only be Na⁺. If these retain their ordinary mobility such as the $35\cdot8$ mhos exhibited in $0\cdot1$ $N$ NaCl (from *International Critical Tables*), their mobility in the presence of the obstruction would be reduced to $0\cdot469 \times 35\cdot8 = 16\cdot8$ mhos.

Hence we have a second independent equation $3\cdot16 = f_1 + 16\cdot8/m_1$. Solving for $m_1$ gives the value $13\cdot2$, indicating that there is one negative charge and therefore one corresponding Na⁺ for every 13 molecules of sodium palmitate. Therefore the concentration of these charges on the fibres is $0\cdot07$ $N_w$. Solving for $f_1$ gives $1\cdot88$ mhos for negative charges and $1\cdot28$ mhos for the positive Na⁺ carriers.

Hence for unobstructed movement the fibres should have a mobility $1\cdot88/1\cdot28 \times 35\cdot8/96500 = 54\cdot5 \times 10^{-5}$ cm./sec./volt/cm., whereas $43\cdot7 \times 10^{-5}$ is found in Table III. The value found is therefore 80 per cent. of that predicted upon the initial assumption that moving sodium ions in the double layer are just as mobile as ordinary sodium ions in $N/10$ sodium chloride. The missing 20 per cent. is within the possible experimental error, and the result substantiates the conclusion that the resistance to motion of these sodium ions cannot differ very much from ordinary sodium ions in solution.

Now that the validity and practicality of this method of approach has been demonstrated, it becomes evident that a large field is open to investigation. A systematic survey of the whole subject and intensive studies of single systems are both highly desirable.

## Summary.

1. A demonstration is given of the complete interchangeability of electrokinetic and electrochemical quantities.

2. Since electrosmosis and cataphoresis can only be forms of electrolysis, and subject to Faraday's laws, it is shown how they may be fully calculated from transport data, whether or not other electrolytes or colloids are present.

3. Examples given include colloidal electrolytes, colloidal electrolytes mixed with curd fibres, both mixed with salts, and curd fibres mixed with simple electrolytes.

4. Electrosmosis is found to be prominent with insoluble curd fibres in solutions of sodium or potassium chloride up to 1 $N$, ζ-potentials of 14 to 65 mv. being indicated, as compared with 39 to 86 mv. for chlorine ion under similarly varied conditions.

5. The surface conductance of 1 $N$ sodium palmitate curd fibres is large, being comparable with the ordinary conductivity of $0\cdot07$ $N$ sodium chloride.

6. Seven per cent. of the molecules in the sodium palmitate fibres are ionised, the current being carried by the negatively charged fibres in the proportion of 3 to 2 as compared with the corresponding sodium ions. These sodium ions possess a mobility almost as great as that of ordinary sodium ions in solution. Likewise, a negative charge upon the curd fibres conducts about as well as if it were on an ordinary chlorine ion.

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# PROPERTIES OF SOLID SOAPS.

BY J. L. BOWEN AND R. THOMAS.

The amount of work on the properties of soaps in solution which has been published in scientific and technical journals is very great and in recent years the experiments of McBain and his co-workers—in particular their Phase Rule experiments—have done much towards placing the soap boiling process on a scientific basis.

A great deal of the research carried out in our laboratories and experimental plant is necessarily closely connected with the above, but from a technical point of view the properties of soap in the solid condition are of equal importance. The amount of published data relating to the physical and physico-chemical properties of solid soap is, however, comparatively small and often only of a qualitative nature. For this reason it is thought that the present paper will prove of greater interest if it is confined to a brief account of work on soap during and after solidification.

It should be remembered that a study of the properties of commercial soaps, which are usually complex mixtures of the salts of various fatty acids, presents quite a different problem to that of " pure " individual soaps. Although in certain cases it is possible to predict broadly the behaviour of the former soaps under a particular set of conditions from a knowledge of the properties of the latter soaps, any such prediction must be accepted with caution ; in many instances the behaviour of mixed soaps is by no means additive.

Further, it will be realised that the physical and physico-chemical properties of any particular brand of commercial soap cannot be defined exactly, since slight variations in the composition of the oils and fats employed, and in manufacturing conditions are unavoidable. The materials used in high-grade soaps are, however, standardised as far as possible and the skilled soap boiler works within very narrow limits, so that the results of work on any one boil or series of boils of the same soap may as a rule be taken as being representative for all practical purposes.

## I. The Effect of the Method of Cooling on the Structure and Properties of Solid Soaps.

The microscopic work of MacLennan [1] who examined soap by means of polarised light, showed that molten soap solidifies on cooling from

[1] *J.S.C.I.,* 5th October, 1923.

two main causes. Fibres grow into and through the fluid crystalline mass and the fluid crystals themselves take on a certain amount of solidity and rigidity. Many features were observed to influence the amount of conversion from fluid crystal to fibre and also the amount of final symmetry which could establish itself in the product. In particular, the rate of cooling was important. Rapid cooling permitted practically no orientation ; much of the original fluid crystal was found to persist as more or less solid irregular lumps, but the whole of the soap was permeated with very fine and very irregular fibres. Slow cooling on the other hand permitted of maximum orientation of both crystals and fibres.

The heterogeneous nature of the structure of soaps—even those made from individual fatty acids—has been repeatedly emphasised. It is very marked with commercial soaps and can often be readily observed in the form of " feather " by ordinary ocular examination. This type of structure is shown in Fig. 5 which is a section of an ordinary household soap.

This heterogeneity not only results from the fact that commercial soaps often contain complex mixtures of fatty acids but also under factory conditions of frame cooling, it is caused by differences in temperature and in the rates of cooling on the inside and outside portions of the soap in the frame. Thus conditions in the centre of a frame of soap where the soap cools slowly would permit of maximum orientation ; at the outside of the frame, cooling is much more rapid, so that less orientation would be expected and the soap would also tend to have a more fibrous structure. Heterogeneity can be avoided to some extent, but by no means prevented, by stirring during cooling and segregation is largely avoided when the soap is cooled rapidly in relatively thin slabs (as in a water cooled frame of the Jacobi type), although differences in structure can still be detected in different parts of such a soap. Toilet soaps which are milled in the solid form several times after drying and are then plodded into bar form have, of course, a much more even structure than frame cooled soaps.

The method of cooling is known to have a marked influence on certain properties of soap, such as colour and hardness. Generally quickly cooled soaps of the Jacobi type are considered to be harder than frame cooled soaps but this does not always appear to be the case. Our work on the hardness of soaps has indicated that while soaps made from certain fat charges show appreciable differences in hardness when cooled (1) slowly in frames and (2) quickly in water jacketed Jacobi coolers, others show little or no difference. The method employed in determining the hardness of soaps will be described later in this paper.

It is interesting to note that the properties of frame cooled genuine soaps are to some extent directional. It has been observed that the shrinkage of such soaps is greater for dimensions horizontally disposed in relation to the original block from which the soaps were cut than for dimensions vertically disposed. It has also been found that vertically cut surfaces radiate heat more slowly than horizontally cut surfaces ; that surface evaporation takes place slightly but undoubtedly less rapidly from vertically cut surfaces than from horizontally cut surfaces and finally that migration of salts from the surface to the interior of the soap is more rapid in a direction normal to a horizontally cut surface than in a direction normal to a vertical surface. This directional effect would appear to be due to the fact that frame cooled soap has a grain-like

structure which generally runs from the top to the bottom of the frame, although in the centre at any rate it follows a somewhat sinuous path with frequent deviations from the vertical. Evidence of such a structure is obtained if a bar of genuine soap is suddenly cooled in liquid air and is then broken up by being struck with a slight sharp blow. The fragments reveal a thin lamellar structure like that of mica. The cleavages are to a very great extent in or nearly in planes that in relation to the original position of the soap in the frame are vertical. A few cleavages normal to these occur, but in general the habit of cleavage favours vertical planes. This directional structure may be connected with the fact that the soap in the frame is crutched after the filling operation, in an up and down direction. When the soap is passing from the filling ducts to the frame its appearance suggests that there is already a great portion of fibre-form soap present, and it is not unlikely that during crutching this may be " brushed " or " combed out " so that it has a tendency to become vertically arranged in the path followed by the crutching tool.

## II. The Contraction of Soap during Cooling.

The experiments which are briefly described in this section were carried out to determine whether there was any noteworthy difference in the rate of contraction of soap during slow and rapid cooling. In one series of experiments cooling from 75° C.-25° C. was carried out over a period of roughly five and a half hours and then to room temperature over night. In the second series the soap was cooled rapidly over a period of about forty-five minutes by placing the experimental apparatus in cold running water.

### Apparatus and Method Employed.

The following is a brief description of the apparatus and method employed. The measurements were made in a form of dilatometer, the wide arm of which was a 250 c.c. cylindrical separating funnel fitted with a ground glass tap and stopper ; the other arm, which contained a column of mercury by means of which the contraction was measured, was a graduated narrow tube.
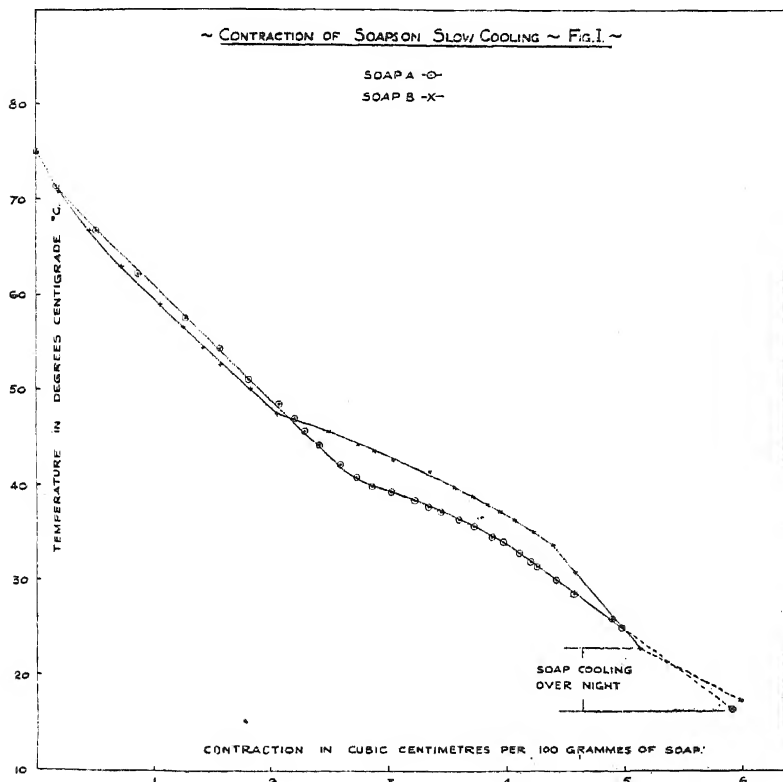
To avoid entrapping air during the filling of the dilatometer with soap the following method was employed. The apparatus was warmed in a steam oven, the stopper was removed and the cylindrical separating funnel in an inverted position was pushed quickly down into a bucket of molten soap. The soap gradually rose in the funnel and was sucked just past the tap by applying gentle suction to the open end of the narrow tube which was outside the bucket. The tap was then closed and the stopper inserted as far as possible by means of a pair of tongs, whilst the neck of the cylinder was still under the soap. The outside of the apparatus was quickly cleaned, the stopper pushed tightly home and the tap opened. A known volume of mercury was next run into the narrow arm of the dilatometer from a burette and the apparatus was then immersed in a bath of hot water at 75° C.-80° C. until the soap had attained the temperature of the bath. In the slow cooling experiments the temperature of the bath was then allowed to fall slowly and readings of the position of the mercury in the narrow arm were made at suitable intervals. As already mentioned a temperature of approximately 25° C. was reached in about five and a half hours, and the soap was then allowed to cool overnight before the final reading was taken. The amount of soap used was determined by weighing.

In the quick cooling experiments, after the soap had attained the

temperature of the hot bath the apparatus was immediately transferred to a cold bath of running water (15°-16° C.) and measurements of the contraction were made after various intervals of time. It was not convenient to record the temperature of the soap during cooling but a rough figure for the temperature at the end of the test was obtained by means of control experiments.

## Results.

The results of typical experiments on two genuine household soaps, one made from a fat charge having a titre of 29° C. (Soap A) and another from a charge having a titre of 30° C. (Soap B) are plotted in graphs (Figs. 1



~ CONTRACTION OF SOAPS ON SLOW COOLING ~ FIG. 1. ~

SOAP A -o-
SOAP B -x-

SOAP COOLING OVER NIGHT

CONTRACTION IN CUBIC CENTIMETRES PER 100 GRAMMES OF SOAP.

and 2). The results have been corrected for the contraction of the glass and mercury during cooling. In the record of the slow cooling experiments the contraction which occurred on cooling from 75° C. to various temperatures is given ; in that of the quick cooling experiments the contraction after different periods of time is recorded.

The weight of soap used in all experiments was approximately 270 gms. but the figures given have been calculated for 100 gms. of soap.

## (a) Slow Cooling.

It will be seen from the graphs that there is a distinct break in the cooling curve of soap A at approximately 40° C. and in that of soap B at 47° C. At these temperatures the commencement of solidification of the soaps from point sources was observed. The curves flatten out over

the solidification period and show a marked increase in the degree of contraction of the soaps. The actual temperatures at which the soaps had completely solidified could not, of course, be ascertained directly but the graphs indicate that solidification was complete at about $31 \cdot 5°$ C. for soap A and $33 \cdot 5°$ C. for soap B. Thereafter the rate of contraction again appears

~CONTRACTION OF SOAPS ON QUICK COOLING.~FIG II.~

SOAP A —⊙—
SOAP B —✕—

TIME IN MINUTES

CONTRACTION IN CUBIC CENTIMETRES PER 100 GRAMMES OF SOAP
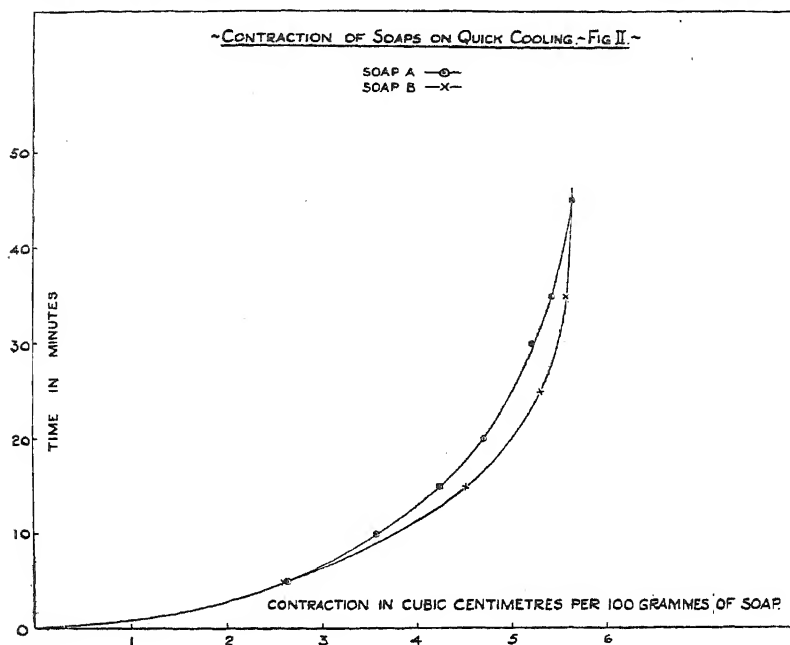
to decrease. The contraction which occurred on cooling overnight is shown by the dotted lines : the figures represented by this portion of the graphs are not too reliable as during this stage the soap showed a tendency to shrink away from the sides of the container.

The initial solidification point of soap B is distinctly higher than that of soap A in spite of the fact that there was little difference in the titres of the fat charges; the former soap, however, contained a higher proportion of hard fats than the latter : 85 per cent. as compared with 70 per cent. The initial solidification temperatures of both soaps are considerably higher than the titres of the fat charges. McBain [2] refers to the work of Krafft and Wigelow which showed that there is a certain parallelism between the initial solidfication temperatures of a sodium soap solution and the melting-point of the pure

TABLE I.

| Condition of Soap. | Soap. | Temperature Range °C. | Coefficient of Cubical Contraction. |
|---|---|---|---|
| Molten soap . . | A | 75-40 | 0·00079 |
| | B | 75-47 | 0·00076 |
| During solidification | A | 40-31·5 | 0·00172 |
| | B | 47-33·5 | 0·00169 |
| Solid soap . . | A | 31·5-25 ? | 0·00108 |
| | B | 33·5-22·5 | 0·00067 |

[2] *The Third Report on Colloid Chemistry*, 1920.

anhydrous fatty acid from which the soap is derived. He points out that this is strictly true for only one concentration ; rather concentrated soap solutions have an initial solidification temperature which is very near the melting-point of the fatty acid, dilute solutions fall much below it whilst highly concentrated solutions come distinctly above it.

The results of the foregoing experiments indicate that the initial solidification temperature of a soap made from a mixture of fats depends largely on the relative amounts of solid and liquid fatty acids present rather than on the titres of the mixed fatty acids.

The coefficients of cubical contraction of the soaps during the different stages of cooling are shown in Table I. The figures relate to the average contraction in c.c. of 1 gm. of soap on cooling 1° C.

### TABLE II.

| Soap. | Contraction in c.c. per 100 gms. Soap. | Coefficient of Cubical Contraction. |
|---|---|---|
| A | 4·96 | 0·00099 |
| B | 4·96 | 0·00099 |

Thus during solidification, the rate of contraction of the soaps was roughly doubled. In the solid state the rate of contraction of soap B was somewhat less than in the liquid state. The figure for soap A in the solid state and the shape of the graph give rise to some doubt as to whether solidification was complete at 31·5° C.; possibly soaps of certain fatty acids present in the mixed fat charge were still in the liquid or semi-liquid condition.

### TABLE III.

| Soap A. Initial Temperature of Soap, 81° C. Temp. of Cooling Water, 16° C. | | Soap B. Initial Temperature of Soap, 77° C. Temp. of Cooling Water, 15° C. | |
|---|---|---|---|
| Time. | Contraction (c.c.). | Time. | Contraction (c.c.). |
| 5 mins. | 2·64 | 5 mins. | 2·59 |
| 10  ,, | 3·56 | 15  ,, | 4·51 |
| 15  ,, | 4·23 | 25  ,, | 5·31 |
| 20  ,, | 4·72 | 35  ,, | 5·58 |
| 30  ,, | 5·22 | 45  ,, | 5·65 |
| 35  ,, | 5·43 | — | — |
| 45  ,, | 5·66 | — | — |

The overall contraction which occurred, when 100 gms. of the soaps was cooled from 75° C. to 25° C. was the same for both soaps (see Table II.) :—

## (b) Quick Cooling.

It will be seen from Fig. 2 (Table III.) that the rate of contraction gradually slowed down : after forty minutes cooling very little further contraction occurred. As already mentioned it was not possible to read the temperature of the soap at the different stages of cooling but control tests showed that when the temperature of the cooling water was 15° C. the temperature at the centre of the soap fell to about 23° C. in forty minutes.

Table IV. gives the contractions of the soaps per 100 gms. which occurred during cooling for forty minutes in cold running water at 15°-16° C. The

### TABLE IV.

| Soap. | Initial Temp. of Soap. | Contraction Per 100 gms. of Soap. | Coefficient of Cubical Contraction. |
|---|---|---|---|
| A | 81 | 5·56 | 0·00090 |
| B | 77 | 5·64 | 0·00097 |

coefficients of cubical contraction have been calculated on the assumption that the final average temperature of the soap was 19° C., *i.e.*, midway between the temperature of the bath and that of the centre of the soap.

6 *

Comparison with the figures given above indicates that for soap A the coefficient of contraction on slow cooling (0·00099) was somewhat higher than for rapid cooling, but for soap B the difference was only slight.   The figures for quick cooling are, however, only approximate and for practical purposes it can be assumed that for these soaps the rate of cooling within the limits examined had no marked effect on the amount of contraction which occurred.

### III. The Hardness of Soaps.

The hardness of soaps is of interest to the soap manufacturer, in connection with cutting, stamping, and handling of soaps, and also in factory control, particularly when products are not made from strictly standard fat charges, or where the oils and fats employed may vary appreciably in their characteristics.   Again, the rate at which the soap wears away in use is not only determined by its solubility, but also by its resistance to rubbing, although the hardness of a soap is not necessarily an index of its durability.

Hardness is essentially a complex phenonemon and its value depends on many factors, the precise nature of which is unknown, so that it cannot be exactly represented by any single numerical quantity.   In order to obtain a measure of hardness in all its phases a number of methods of testing would therefore have to be employed.   Such a procedure would be impracticable from a technical point of view, not only because of the time involved but also because of the difficulty of obtaining identical samples of soap for each individual test.   As indicated in an earlier section of this paper, bars of genuine soap, particularly those which have been frame cooled, often show considerable variations in their structure, and consequently in their hardness, throughout the length of the bar.

In developing a test which would not only be of use for experimental work but also for factory control, it was therefore of first importance that the apparatus used should be capable of testing a relatively large surface of soap in a short time.   A number of methods have been suggested for measuring the hardness of plastic materials, such as soap, and of these one in which the resistance offered by a soap to a cutting wire (*i.e.*, its sectility) is determined, appeared to be most promising. The sectility of the soap will be referred to in this paper as its hardness.

### Description of Machine and Method of Testing.

The machine devised for our purpose is shown in the accompanying photographs (Figs. 3 and 4) : the measurement recorded is the resistance in pounds offered to a cutting wire by a bar of soap which moves forward against the wire at a constant standard rate.   The following is a very brief description of the manner in which the test is carried out :—

A bar of soap of the required dimensions is placed in a fixed position on a carriage which runs on rails and which is drawn forward at constant speed of about 10 ins. per minute, by means of an electric motor and suitable attachments.   The front end of the soap is in contact with a cutting wire fixed across the front of a frame which also runs on rails and moves in the same direction as the soap carriage.   The opposite end of the frame is attached to a calibrated spring, or battery of springs, the other ends of which are secured to a fixed column.   As the soap carriage moves forward, the frame moves with it—the wire being in contact with the front of the bar of soap—and the springs are gradually extended until the force they exert is sufficient to cut the soap.   If the hardness of the soap does not vary throughout its length, the position of the frame, and therefore the extension of the spring, will thereafter remain constant while the soap
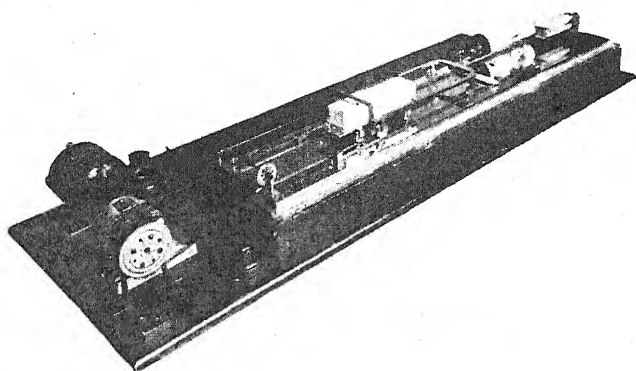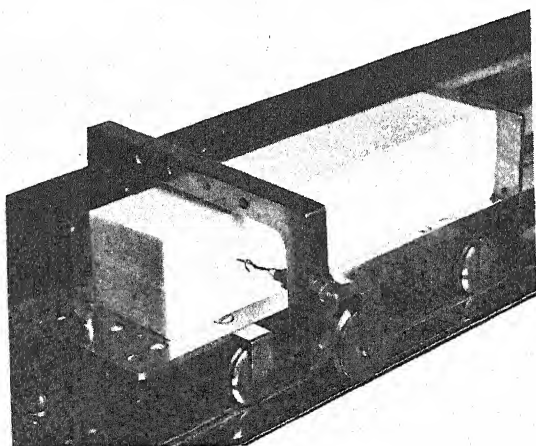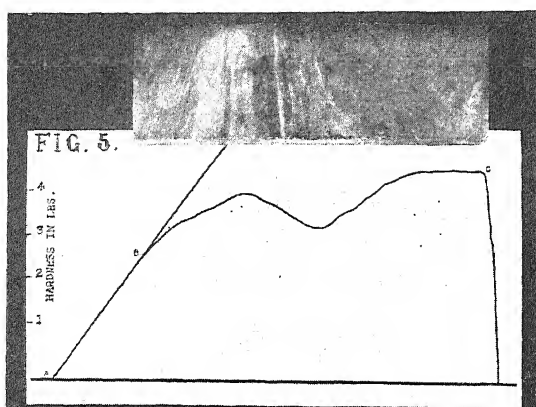
FIG. 3.



FIG. 4.

FIG. 5.

HARDNESS IN LBS.

*See page* 171.



EFFECT OF SMALL AMOUNTS OF INORGANIC SALTS
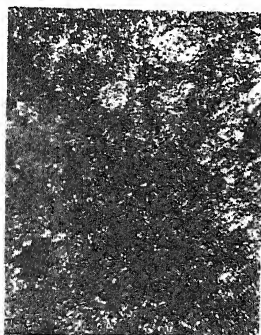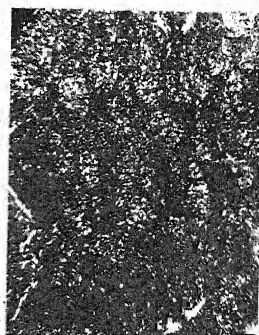ON STRUCTURE OF SOAP.

FIG. 9.

CONTROL

0·5% $Na_2CO_3$
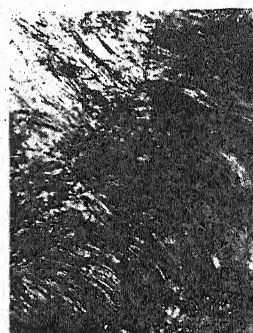
1·0% $Na_2CO_3$

1·5% $Na_2CO_3$

2·0% $Na_2CO_3$

[*See page* 176.

is cut. The extension of the spring throughout the test is recorded auto-matically by means of an attachment to the frame which records on a graph paper fixed around a revolving drum, the peripheral speed of which is roughly the same as that of the soap carriage.

A graph for a bar of genuine soap—which was selected because of the marked variation in its structure, *i.e.*, " feather "—is given in Fig. 5, and the cut surface of the bar is shown in the photograph above.

The gradual extension of the spring before the soap is cut is represented on the graph by the line AB. At B the force exerted by the spring is sufficient to cut the soap, and the line BC then records the hardness of the specimen. The variation of hardness with the structure of the soap is clearly seen when the graph is compared with the photograph of the cut section of the bar. Apart from the advantages already mentioned, this method has therefore the additional merit that after the measurement has been made any area of the cut samples can be examined in relation to the hardness shown on the graph.

The use of a battery of springs enables the machine to be used over a wide range of hardness. As illustrations of the range of hardness, some genuine soaps which are marketed have a hardness as low as 2 to 3 lbs.



FIG. 6

EFFECT OF SKIN FORMATION

A. END SKIN.
B. NO SKIN.     TEMP. 20°C.
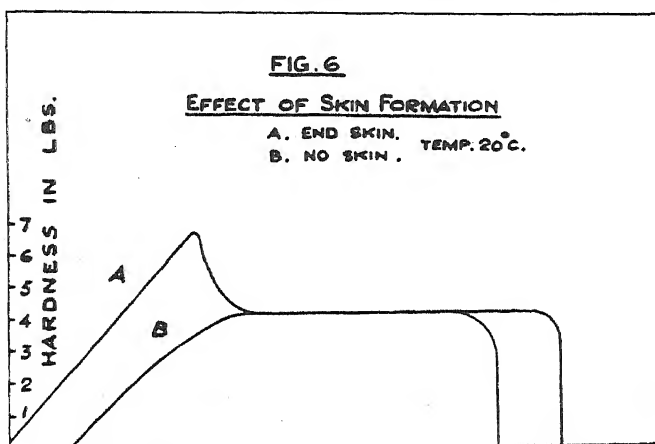
at ordinary temperature, whilst milled toilet soaps may give figures of 12 to 14 lbs. or higher.

The change in hardness due to skin formation is shown in Fig. 6, curve A, which was obtained for a " filled " soap that had been exposed to the atmosphere for twenty days. In determining skin hardness the end skin only is tested, the side skins being removed to give a billet of standard width before the measurement is made. The peak on the curve A is characteristic of skin hardness. Curve B represents the interior hardness of a bar of the same soap after the same period of storage. It will be seen that the flat portions of the two curves coincide so that if the bar is sufficiently long curve A is a record of both skin and interior hardness.

For the determination of hardness the following factors must be standardised :—

1. The Width of the Soap Billet.
2. The Diameter of the Cutting Wire.
3. The Speed of the Soap Carriage.
4. Temperature.

As illustrating the effect of the last factor one example may be quoted in which the hardness of a sample of genuine soap tested was decreased to one-third when the temperature was increased from 10° C. to 38° C.

## Applications.

Two applications of the hardness machine will now be briefly described.

### (a) The Hardness of Soaps in Relation to the Titre of their Fat Charge.

For economic reasons the possibility of partial or complete substitution in the fat charge of a soap of one oil or fat by another without markedly affecting the properties of the soap is of great interest to the soap manufacturer, and the hardness of the soap is one of the main properties which have to be considered when such a change is contemplated.

Broadly the hardness of a soap at any particular fatty acid content * and temperature will increase with the titre of the fatty acids, although the hardness of soaps made from different mixtures of fats having the same titre may vary considerably. The results of an investigation of the hardness of soaps made from mixtures of tallow and palm oil, indicated, however, that when two fats are mixed in varying proportions the hardness of the soap is determined by the titre of the fatty acids in the mixed fat charge.

Table V. shows the titres of the mixed fatty acids and the hardnesses of soaps made from them.

TABLE V.

| Palm Oil. | Tallow. | Titre of Fatty Acids, 50° C. | Hardness of Soap, lbs. | |
|---|---|---|---|---|
| | | | Slowly Cooled. | Quickly Cooled. |
| 100 per cent. | — | 45·5 | 7·9 | 7·8 |
| 75 ,, ,, | 25 per cent. | 42·7 | 5·8 | 5·4 |
| 50 ,, ,, | 50 ,, ,, | 42·3 | 5·6 | 5·1 |
| 25 ,, ,, | 75 ,, ,, | 43·3 | 5·7 | 5·7 |
| — | 100 ,, ,, | 43·5 | 6·0 | 5·8 |

The hardness results are in all cases the average of a number of determinations which were carried out at 20·5° C. on the slowly cooled soaps, and 19·5° C. on the quickly cooled soaps.

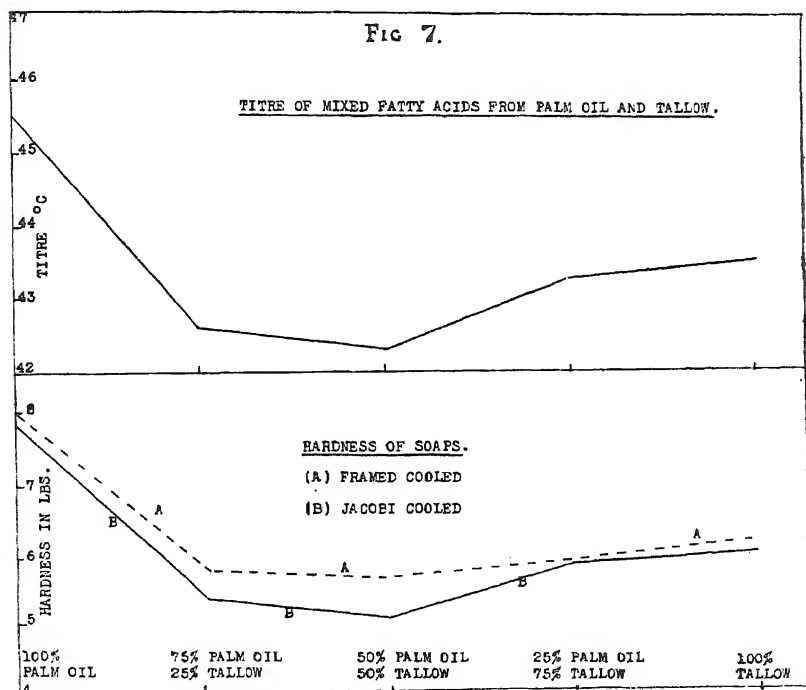Curves in which the percentages of palm oil and tallow in the fat charges are plotted against (1) the titre of the fatty acids, and (2) the hardness of the soap in pounds, are shown in the accompanying graph, Fig. 7. It will be seen that the general shapes of the curves are very similar, and that soaps made from the mixed fat charges are all softer than those made from palm oil or tallow alone. The general order of hardness was not changed by weathering the soaps under ordinary atmospheric conditions for periods up to ten days, or by increasing the temperature of the soaps to approximately 32° C. In connection with the exposure of the soaps at room temperature it was noted, however, that the soap made from tallow alone hardened at a somewhat quicker rate than the soap made from palm oil alone, and this appeared to be due to the quicker rate of drying of the former soap. After weathering for some time the tallow soap, which originally had a fatty acid content of 60·8 per cent., had dried up to 74·19 per cent. on the surface and to 64·09 per cent. in the interior of the billet. The palm oil soap, which originally had a fatty acid content of 60·17 per cent., dried to 69·94 per cent. on the surface and to 60·53 per cent. in the interior of the billet.

The results of the hardness measurements also showed that on the whole the frame cooled soap had much the same hardness as the corresponding Jacobi cooled soap, but, as already pointed out, this is not true of all soaps.

* *i.e.*, fatty acid combined as soap.

## (b) The Effect of Electrolytes on the Hardness of Soaps.

It is generally considered that the hardness of a soap is chiefly con-
ditioned by the presence of curd fibres, but it also depends to a certain
extent on the development of soap gel.    The  marked effect of salts
on the hydration and solubility of soap and on the viscosity of soap solu-
tions has been clearly demonstrated by the work of McBain and others.
That these salts have also a considerable influence on the hardness of
soap is also known, but most of the evidence available is of a qualitative
nature.   Experiments were therefore undertaken to investigate quan-
titatively the effect of relatively low percentages of various salts on the
hardness of commercial soaps.    The salts in fine powder form * were
thoroughly mixed into the molten soaps in a crutcher, after which the
soaps were cooled in frames.    Special care was taken to carry out the



FIG 7.

TITRE OF MIXED FATTY ACIDS FROM PALM OIL AND TALLOW.

HARDNESS OF SOAPS.

(A) FRAMED COOLED

(B) JACOBI COOLED

framing of the soaps under as nearly as possible identical conditions, and
the billets of the various soaps taken for test were cut from corresponding
positions in the frames.    The effects of the addition of sodium chloride,†
sodium carbonate and sodium sulphate to a genuine 63 per cent. T.F.M.
household soap are shown in Fig. 8.    It will be seen that with increasing
concentrations of all three salts the hardness of the soap falls to a minimum,
and thereafter increases.    With sodium carbonate and sodium sulphate the
decrease in hardness is very marked, amounting to approximately 3·3 lbs.
and 4·9 lbs. respectively for concentrations of salts between 1 and 2 per
cent.    The concentrations of these and of other salts at the point of
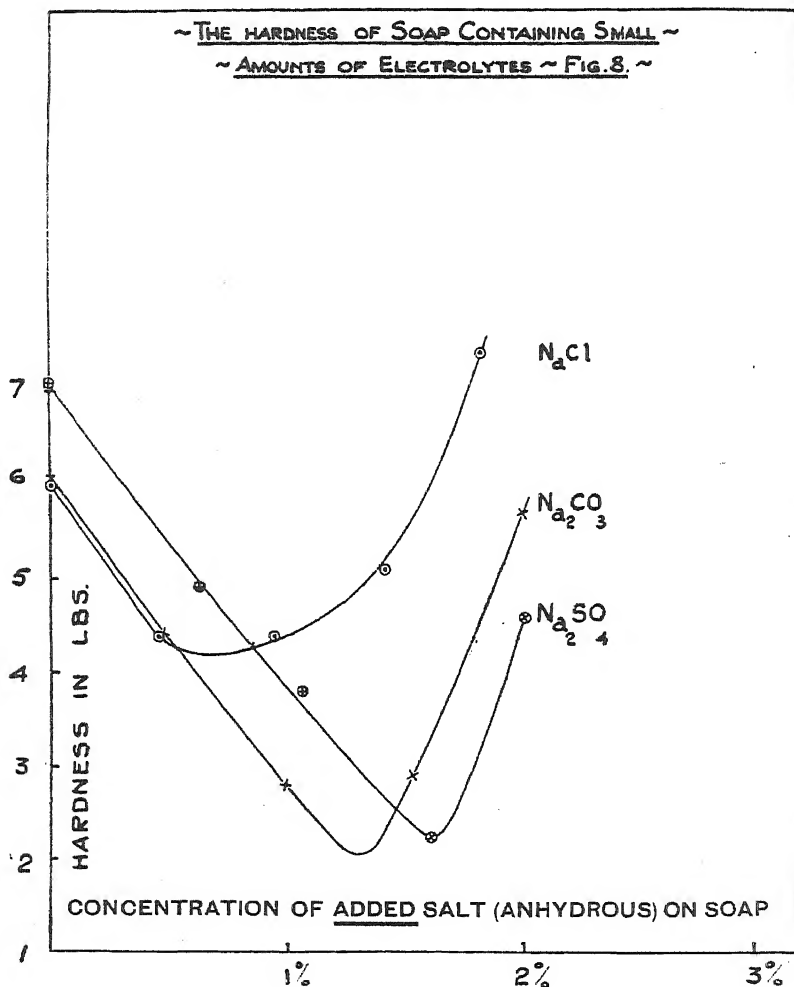
* Sodium chloride, sodium carbonate and sodium sulphate were added in
a practically anhydrous condition : the other salts contained water of hydration
which amounted to roughly 30-35 per cent. of their weight.
    † In excess of that present in the soap from the pan.

minimum hardness are given in the table below, in the fourth column of which is recorded the ratio,

$$\frac{\text{concentration of added anhydrous salt at minimum hardness}}{\text{molecular weight of salt}}.$$

Figures are given for a genuine household soap base and for a toilet soap base, both of which were obtained from ordinary production boils. In neither case was it possible to use the soap base from one boil only for



~ THE HARDNESS OF SOAP CONTAINING SMALL ~
~ AMOUNTS OF ELECTROLYTES ~ FIG. 8. ~

$N_aCl$

$N_{a_2}CO_3$

$N_{a_2}SO_4$

HARDNESS IN LBS.

CONCENTRATION OF ADDED SALT (ANHYDROUS) ON SOAP

1%  2%  3%

our tests, but the fatty acid contents of the household base only varied over a range 62·7 per cent. to 63·5 per cent., and the two boils of toilet base had fatty acid content of 63·9 and 64·4 per cent. respectively.

Control experiments indicated that the above differences in fatty acid content had no marked influence on the hardness of the soaps. The salt contents of the former soaps ranged from 0·49 per cent. to 0·53 per cent. NaCl, and the latter soaps contained 0·33 per cent. and 0·39 per cent. respectively.

TABLE VI.

| Salt. | Concentration of Added Salt (Anhydrous) at Point of Minimum Hardness. Per Cent. on Soap | Molecular Weight of Salt. | Ratio:— Concentration at Minimum Hardness. Molecular Wt. |
|---|---|---|---|
| *Genuine Household Soap Base.* | | | |
| NaCl . . . . . | 0·63 | 58·5 | 0·011 |
| Na₂CO₃ . . . . | 1·30 | 106·0 | 0·012 |
| Na₂SO₄ . . . . | 1·62 | 142·0 | 0·011 |
| Na₂S₂O₃ . . . . | 1·34 | 158·0 | 0·0085 |
| Na₂B₄O₇ . . . . | 2·00 | 202·0 | 0·010 |
| Commercial trisodium phosphate 51·46 Na₃PO₄, 19·35 Na₂CO₃. Av. molecular weight 148·2 . . . | 1·72 | 148·2 | 0·012 |
| *Toilet Soap Base.* | | | |
| NaCl . . . . | 0·55 | 58·5 | 0·009 |
| Na₂CO₃ . . . . | 0·9 | 106 | 0·0085 |

It will be seen that for both soaps the ratio,

$$\frac{\text{concentration of added anhydrous salt at minimum hardness}}{\text{molecular weight of salt.}},$$

is roughly the same for all the salts ; also as the mixture of trisodium phosphate and sodium carbonate gives a similar ratio, the effect of these salts would appear to be additive. With the exception of borax a sharp minimum of the type shown in the graph was reached : the individual measurements for this salt and for caustic soda which also gave a very flat minimum, are recorded in Table VII.

TABLE VII.

| Anhydrous borax (per cent. on soap) . | Nil | 0·52 | 1·11 | 1·48 | 2·14 | 2·7 |
|---|---|---|---|---|---|---|
| Hardness in lbs. . . . . | 5·2 | 4·1 | 3·4 | 3·2 | 3·1 | 3·2 |
| NaOH as Na₂O (per cent. on soap) . | Nil | 0·02 | 0·06 | 0·10 | 0·15 | — |
| Hardness in lbs. . . . . | 6·3 | 6·6 | 5·6 | 5·5 | 5·4 | — |

It will be seen that the presence of 0·02 per cent. free caustic alkali as Na₂O causes a slight increase in the hardness of the soap, but thereafter there is a definite decrease in hardness with increasing caustic concentration.

It is interesting to note that McBain and Pitter[3] state that in the salting out of soap " Perhaps the most unexpected feature . . . is that, as a first approximation, the salts do not replace each other equivalent for equivalent but rather mol. for mol. irrespective of their valency," and also that " The effects in a mixture of electrolytes are additive."

Some of our experiments indicated that at still higher concentrations of added salts the hardness of the soap again rises to a maximum figure, and thereafter begins to fall again. Thus, on the gradual addition of sodium thiosulphate to a genuine household soap the hardness first decreased

[3] " The relative concentrations of various electrolytes required to salt out soap solutions," *J.C.S.*, 893, 1926.

from an original hardness of 4·8 lbs. to 2·7 lbs. at a concentration of about 0·99 per cent., after which it increased to 5·3 lbs. at a concentration of 2·50 per cent. and then fell to 4·6 lbs. at a concentration of 3 per cent. On the addition of sodium chloride to a toilet soap base the hardness fell from an original figure of 7·9 lbs. to 6·2 lbs. at a concentration of 0·55 per cent. salt, then rose to a hardness of 11·3 lbs. at a concentration of 1·61 per cent. salt, and fell again to 8·6 lbs. at a concentration of 1·71 per cent. salt.

Attempts to follow the alterations in the structure of some of the soaps with the addition of increasing amounts of salt were made by examining thin sections microscopically, by means of transmitted polarised light. The accompanying photographs (Fig. 9) of soaps containing from 0-2 per cent. of added sodium carbonate indicate distinct changes in structure. The soap without added carbonate had the usual large crystalline structure of this genuine soap.   The soap containing 0·5 per cent. sodium carbonate had a somewhat smaller and more fibrous structure, which was even more marked in the soap containing 1 per cent. sodium carbonate.   The addition of 1·5 per cent. and 2 per cent. sodium carbonate altered the structure of the soap completely : the fibrous appearance had entirely disappeared and the polarised areas were very small and nodular compared with those of the soap without additions.   Exactly the same changes, although not quite to the same extent, were noticed when sodium chloride was added to this genuine soap.

## IV. The Migration of Salts in Solid Soap.

Most genuine soaps and toilet soaps contain small quantities of salts, mainly sodium chloride and sodium carbonate—the latter often being formed by reaction of atmospheric carbon dioxide with a small amount of free caustic alkali—which are not removed during the washing and settling treatments in the pan.   Filled soaps may contain appreciable quantities of salts such as sodium carbonate and sodium silicate.

Under certain conditions the salts present in solid soap may crystallise on the surface of the bar and on drying give rise to the phenomenon known in the soap trade as " efflorescence " or " bloom."

The analysis of various parts dissected out from old tablets of laundry soap and also from plodded toilet soap suggested a degree of heterogeneity in the distribution of the " water soluble matter other than soap."   In particular the sodium chloride was not found to remain uniformly distributed throughout the tablet, but a great part of it had accumulated near the centre and comparatively little remained near the surfaces.[*] The more or less plastic, opaque soap forming the interior of an old tablet of a genuine household soap yielded 0·4 per cent. chlorine, whilst the surrounding soap, harder and translucent, had only 0·09 per cent.   An old tablet of plodded toilet soap gave 0·3 per cent. and 0·15 per cent. chlorine for material near the centre and near the surface respectively. It was decided to follow up these observations as it was considered that the elucidation of the causes of such apparent movement of the " water soluble salts other than soap," within the mass of the bar or tablet might contribute towards an understanding of the phenomenon of efflorescence.

Early attempts to trace the migrations quantitatively produced some interesting data of which an example is given.   Large cubes of a soap made from a palm oil and rosin charge run down to 32 per cent. saponified fatty acids concentration with solutions of alkaline silicate of soda and carbonate of soda were kept at room temperature until some 45 per cent. of the original weight had been lost and there was an efflorescence upon

* Confirmation of these observations will be found in the work of Kristen (*Seifens. Z.*, 665, 1927), and in the results of later experiments by Mikumo (*J. Soc. Chem. Ind., Japan*, 116B, 1931).

the surfaces.   This condition was established at the expiry of ten months. Samples were dissected out and analysed.

|  | Original Soap. Per Cent. | Centre. Per Cent. | Intermediate. Per Cent. | Near Surface. Per Cent. |
|---|---|---|---|---|
| Saponified fatty acids    .    . | 32·0 | 56·2 | 58·5 | 59·2 |
| Parts per 100 parts of saponified fatty acids :— |  |  |  |  |
| Chlorine    .    .    .    . | 0·28 | 0·77 | 0·60 | 0·25 |
| Silica (total)    .    .    . | 8·10 | 4·28 | 4·03 | 9·08 |
| ,,    (insoluble) .    .    . | — | 1·65 | 1·50 | 2·05 |
| ,,    (soluble)   .    .    . | — | 2·63 | 2·53 | 7·03 |
| $Na_2O$ as carbonate    .    . | 1·39 | 1·61 | 1·45 | 1·35 |
| ,,    ,, silicate  .    .    . | — | 1·42 | 1·37 | 2·84 |

From such data—of which a great deal was established—it appeared to be correct to conclude (1) that sodium chloride migrated away from the surfaces and towards the central parts of the soap, (2) that sodium carbonate had a similar but not so strong habit, and (3) that sodium silicate migrated in the opposite direction.

Early experiments made it clear that in order to trace quantitatively the migrations of salts in soap it was necessary that the three or more samples dissected out should include the whole of the soap under examination.

The following is an account of typical experiments which were carried out in order to investigate the migration of sodium chloride and sodium carbonate when present in soap at various concentrations, both separately and in admixture.   The soap employed was made from a charge consisting of 75 per cent. palm oil and 25 per cent. rosin : it was very thoroughly washed and settled during manufacture.

The soap was neutralised in the crutcher with palm and rosin acids, and small additions of sodium chloride and/or sodium carbonate were carefully mixed in.   The soaps were cut into billets (6 ins. $\times$ 2½ ins. $\times$ 2 ins.) and stored under equal conditions.

The quantities of the salts used in the experiments are given in the table below :   they are expressed on the total water present in the soap which was approximately 33 per cent .to 34 per cent. before storage, and of the order of 16 per cent. to 22 per cent. in the centre of the soap, and 12 per cent. to 15 per cent. near the surface of the soap after storage.

CONCENTRATION OF SALTS EXPRESSED ON WATER CONTENT.

| Series I. | | Series II. | | Series III. | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| NaCl. | | $Na_2CO_3$. | | (a) | | | (b). | | |
|  |  |  |  | Mixtures of NaCl and $Na_2CO_3$. | | | | | |
| Soap Ref. | Per Cent. NaCl. | Soap Ref. | Per Cent. $Na_2CO_3$. | Soap Ref. | Per Cent. NaCl. | Per Cent. $Na_2CO_3$. | Soap Ref. | Per Cent NaCl. | Per Cent. $Na_2CO_3$. |
| (1) | 3·16 | (5) | 2·61 | (9) | 0·19 | 0·40 | (14) | 2·45 | 0·52 |
| (2) | 2·34 | (6) | 1·87 | (10) | 0·22 | 0·56 | (15) | 1·56 | 1·15 |
| (3) | 1·55 | (7) | 1·19 | (11) | 0·31 | 0·50 | (16) | 0·85 | 1·76 |
| (4) | 0·81 | (8) | 0·68 | (12) | 0·50 | 0·60 | (17) | 0·07 | 0·03 |
| | | | | (13) | 0·78 | 0·48 | | | |

PROPERTIES OF SOLID SOAPS

It should be noted that a small percentage of sodium carbonate (ca. 0·3 per cent.) was unavoidably present in all the soaps of Series I. and a small percentage of sodium chloride (ca. 0·05 per cent.) in the soaps of Series II.

TABLE VIII.—SERIES I.—MIGRATION OF SODIUM CHLORIDE.

| Soap Ref. | Section. | Per Cent. NaCl on Water Present. | |
|---|---|---|---|
| | | Dissected Part. | True Average |
| (1) | Near surface | 13·39 | |
| | Intermediate | 8·61 | 9·04 |
| | Centre | 6·51 | |
| (2) | Near surface | 6·02 | |
| | Intermediate | 7·76 | 7·49 |
| | Centre | 6·75 | |
| (3) | Near surface | 2·54 | |
| | Intermediate | 4·15 | 4·31 |
| | Centre | 5·06 | |
| (4) | Near surface | 0·87 | |
| | Intermediate | 1·39 | 2·17 |
| | Centre | 3·36 | |

In Series III. (a) it was intended that the sodium carbonate content should be the same in all the soaps references 9 to 13 and that the sodium chloride content should gradually increase throughout the series: it will be seen, however, that the concentration of the former salt in the finished soap varied from 0·40 per cent. to 0·60 per cent.

In Series III. (b) the sodium chloride content was gradually decreased throughout the series of soaps references 14 to 16, and the sodium carbonate content was increased. Soap reference 17 was the control soap and contained no addition.

On the expiry of twenty weeks the billets of soap were dissected and analysed. A scheme of dissection had been worked out enabling samples of approximately equal weights to be prepared, a complete billet being used in each case. Thus "near surface" samples including all edges and corners, "intermediate" samples and "centre" samples of 130 gms. to 140 gms. each were taken; the whole of each sample was dissolved and aliquot parts of the (hot) solutions were taken for the various analytical determinations. Apart from water, much of which was, of course, evaporated during storage, the whole of the substance originally present in each billet was accounted for with good concordance.

The analytical data showing the various amounts of the salts in the three sections of each billet are given in the above and following tables.

The "true average" values were obtained by quantifying the data for the amount of migrant in the dissected parts, together with the actual weights of these parts.

TABLE IX.—SERIES II.—MIGRATION OF SODIUM CARBONATE.

| Soap Ref. | Section. | Per Cent. Na₂CO₃ on Water Present. | |
|---|---|---|---|
| | | Dissected Part. | True Average. |
| (5) | Near surface | 4·01 | |
| | Intermediate | 8·07 | 7·62 |
| | Centre | 8·56 | |
| (6) | Near surface | 2·42 | |
| | Intermediate | 5·00 | 5·23 |
| | Centre | 6·65 | |
| (7) | Near surface | 1·81 | |
| | Intermediate | 3·18 | 3·36 |
| | Centre | 4·13 | |
| (8) | Near surface | 0·81 | |
| | Intermediate | 1·54 | 1·16 |
| | Centre | 0·99 | |

It will be seen that the relative migration of salt towards the centre

of the tablet was most marked in the soap containing the smallest amount of salt. Soap (1), which had the highest salt concentration, was in a class alone, concentration of the salt having occurred in the surface and intermediate layers : it alone of all the samples showed a surface crystallisation of sodium chloride in minute perfect cubes. The results indicate that in this case evaporation has been too rapid, crystallisation having occurred at the surface before the concentration of the solution could be reduced below saturation by inward migration of the salt.

When this soap was in the crutcher it differed markedly from all the others in the series. It was a thin gruel-like material but it set up well in the frame, and analytical data on samples from different parts of the frame suggested a good degree of homogeneity. Microscopical examination of thin sections of the solid soap showed that the precipitated or coagulated particles present were smaller than those in the other soaps.

The progress of diffusion may be visualised from the above data. In all of the soaps the sodium carbonate migrated towards the centre. The effect of the original concentration of carbonate in the soap on the amount of migration which occurs is not very apparent in this series ; migration was most marked in soap (6) and least in soap (8) containing the smallest amount of carbonate.

TABLE X.—SERIES III (a).—Migration of Mixtures of Sodium Chloride and Sodium Carbonate.

| Soap Ref. | Section. | Per Cent. NaCl and $Na_2CO_3$ on Water Present. | | | |
|---|---|---|---|---|---|
| | | NaCl. | | $Na_2CO_3$. | |
| | | Dissected Part. | True Average. | Dissected Part. | True Average. |
| (9) | Near surface . . | 0·39 | | 0·65 | |
| | Intermediate . . | 0·27 | 0·55 | 1·21 | 1·28 |
| | Centre . . . | 0·82 | | 1·64 | |
| (10) | Near surface . . | 0·26 | | 0·92 | |
| | Intermediate . . | 0·28 | 0·63 | 1·62 | 1·54 |
| | Centre . . . | 1·09 | | 1·70 | |
| (11) | Near surface . . | 0·48 | | 0·96 | |
| | Intermediate . . | 0·49 | 0·92 | 1·46 | 1·46 |
| | Centre . . . | 1·08 | | 1·67 | |
| (12) | Near surface . . | 0·87 | | 1·66 | |
| | Intermediate . . | 0·73 | 1·44 | 1·34 | 1·81 |
| | Centre . . . | 2·20 | | 1·98 | |
| (13) | Near surface . . | 1·01 | | 1·44 | |
| | Intermediate . . | 1·44 | 2·02 | 1·32 | 1·53 |
| | Centre . . . | 2·83 | | 1·49 | |

The results indicate that the diffusion of sodium carbonate is restrained progressively by the increased addition of sodium chloride. This can be more readily visualised from Table XI., in which the figures for the dissected parts are expressed as a percentage of the true average.

The significance of these figures with reference to the efflorescence of soap is apparent. Freedom from crystallisation on the surface of the soap is desired and thus the more effectively diffusion removes the fillings from near the surface, the less is the danger of undesirable appearances.

Obviously soap 9 is the most favourable from this point of view, and soap 13 the most dangerous.

TABLE XI.

| Soap Ref. | Original Per Cent. NaCl on Water Content. | $Na_2CO_3$ Per Cent. on True Average. | | |
|---|---|---|---|---|
| | | Near Surface. Per Cent. | Intermediate. Per Cent. | Centre. Per Cent. |
| 9 | 0·19 | 50·35 | 94·31 | 127·9 |
| 10 | 0·22 | 59·94 | 105·6 | 110·5 |
| 11 | 0·31 | 66·07 | 100·2 | 114·4 |
| 12 | 0·50 | 91·77 | 74·26 | 109·4 |
| 13 | 0·78 | 94·06 | 86·17 | 97·4 |

TABLE XII.—SERIES III (*b*).—MIGRATION OF MIXTURE OF SODIUM CHLORIDE AND SODIUM CARBONATE.

| Soap Ref. | Section. | Per Cent. NaCl and $Na_2CO_3$ on Water Present. | | | |
|---|---|---|---|---|---|
| | | NaCl. | | $Na_2CO_3$. | |
| | | Dissected Part. | True Average. | Dissected Part. | True Average. |
| 14 | Near surface .   . | 5·97 | | 1·33 | |
| | Intermediate .   . | 7·32 | 6·99 | 1·86 | 1·41 |
| | Centre .   .   . | 5·05 | | 0·72 | |
| 15 | Near surface .   . | 3·85 | | 3·22 | |
| | Intermediate .   . | 4·65 | 4·76 | 5·23 | 4·05 |
| | Centre .   .   . | 4·53 | | 2·75 | |
| 16 | Near surface .   . | 1·48 | | 4·67 | |
| | Intermediate .   . | 1·95 | 2·33 | 6·15 | 6·05 |
| | Centre .   .   . | 2·83 | | 5·77 | |
| 17 (Control) | Near surface .   . | 0·13 | | 0·79 | |
| | Intermediate .   . | — | | — | |
| | Centre .   .   . | 0·15 | | 0·59 | |

The restraint of the migration of sodium carbonate as the concentration of this salt decreased and the concentration of sodium chloride increased, is here strikingly demonstrated. Soap 14, which after storage contained more sodium carbonate near the surface than at the centre, originally contained 2·45 per cent. (on total water) of sodium chloride and 0·52 per cent. sodium carbonate. Soap 16, which after storage contained more sodium carbonate at the centre than near the surface, originally contained only 0·85 per cent. of sodium chloride and 1·76 per cent. of sodium carbonate. On the other hand, increasing the amount of carbonate and decreasing the concentration of chloride appears to have increased the tendency of the latter salt to migrate to the centre.

Table XIII. expresses these figures as a percentage of the true average concentration.

TABLE XIII.

| Soap Ref. | Original Per Cent. NaCl and $Na_2CO_3$ on Total Water. | | NaCl Per Cent. and $Na_2CO_3$ Per Cent. on True Average. | | |
|---|---|---|---|---|---|
| | | | Near Surface. | Intermediate. | Centre. |
| 14 | NaCl | 2·45 | 85·42 | 104·67 | 72·16 |
| | $Na_2CO_3$ | 0·52 | 94·69 | 132·05 | 51·42 |
| 15 | NaCl | 1·56 | 80·71 | 97·69 | 95·00 |
| | $Na_2CO_3$ | 1·15 | 79·54 | 129·27 | 67·99 |
| 16 | NaCl | 0·85 | 63·43 | 83·69 | 121·56 |
| | $Na_2CO_3$ | 1·76 | 77·14 | 101·66 | 95·39 |

From the preceding results it would appear that the main processes involved in the phenomena of diffusion in solid soaps containing small percentages of soluble inorganic salts are : the evaporation of water from the surface of the soap, concentration of fillings near the surface, and consequent migration of the fillings to the centre of the soap. After a certain amount of water has been lost by evaporation there may also be a recession of solution as a whole from the surface of the soap. If evaporation takes place too quickly for diffusion to measurably equalise it, the concentration of the fillings may exceed saturation value and deposit crystals on the surface of the soap, which may dessicate and effloresce. It is thought that the diffusing salts—which are present in solution or perhaps in a gel—move through what may be termed channels or crevices in the soap which are bounded either by soap fibres or by soap in the fluid crystal condition. The tendency for such a structure to be directional has already been referred to.

The retarding influence on diffusion in solution of one salt upon another is known, and it would appear that the same phenomenon occurs in solid soaps containing electrolytes.

Finally, a brief reference will be made to soaps containing sodium silicate and heavily filled soaps. As already indicated it has been found that silicate migrates towards the surface of the soap : this may be accounted for in the following manner—when the surface of an aqueous solution of sodium silicate is exposed to air containing carbon dioxide, a reaction takes place, sodium carbonate (and/or bicarbonate) and an insoluble silicon compound being formed. In the immediate vicinity of the exposed surface there is therefore (momentarily) a *decrease* in the amount of sodium silicate in solution and an *increase* in the amount of sodium carbonate in solution. Thus it is to be expected there will be *diffusion in opposite directions*, sodium silicate moving towards the exposed surface and sodium carbonate moving away from the exposed surface, the tendency in both cases being to establish uniform concentrations of the compounds throughout the whole of the solution.

In contradistinction to soaps containing only relatively small amounts of electrolytes, in very heavily filled soaps a concentration of " substances other than soap " occurs in the surface layer when the soap has been stored for some time. In such soaps the amount of water in the skin section after drying is, as a rule, not nearly sufficient to maintain the salts in solution, whilst the water in the intermediate and core sections may be regarded as approaching saturation with the inorganic salts present. A possible explanation of this outward migration may be

found in the following theory advanced in connection with rhythmic precipitation by Liesegang :—[4]

" In connection with the theory advanced by Wilhelm Ostwald for the rhythmic precipitation of silver chromate, one can suggest also in this case that the salt on progressive drying, first reaches a state of super-saturated solution, and that afterwards the metastable limit is reached at one place, where the transition into the solid state occurs without the presence of nuclei. Then a portion of the supersaturated solution diffuses from the neighbourhood to the nuclei thus formed, where it becomes solidified as well. . . . "

Microscopic observations of thin sections of these heavily filled soaps mounted in paraffin led to the interesting observation that when commercial soaps are treated with certain hydrocarbon oils, globules of aqueous liquor are separated in greater or less quantity, depending roughly on the amount of aqueous liquor available. Efforts made to effect a complete quantitative separation of such liquor from heavily filled soaps were not successful, only about 50 per cent. of the total liquor present being removed as globules when these were allowed to settle by gravity. The liquor removed, however, had a composition remarkably similar to that of the " substances other than anhydrous soap " initially present in the soap. This suggested that the soap—which in the presence of such high concentrations of fillings is probably present in curd fibre form—is not hydrated.

Further experiments in which a different technique was employed for the separation of the liquid did not, however, confirm this view. Very thin shavings of soap were cut on the microtome, steeped in petrol ether and pressed between blotting paper. The steeping and drying were repeated three times and the residual shavings were analysed. In one experiment the total fatty matter figure was raised from 19·4 per cent. to 58·4 per cent. by this treatment, and the composition of " substances other than anhydrous soap " remaining in the soap altered as in Table XIV.

TABLE XIV.

| | Before Treatment. | After Treatment. |
|---|---|---|
| $Na_2O$ (other than as soap) . | 4·63 | 4·33 |
| Soluble $SiO_2$ . . . | 3·42 ⎱ 3·48 | 2·58 ⎱ 3·32 |
| Insoluble $SiO_2$ . . . | ·06 ⎰ | ·74 ⎰ |
| NaCl . . . . | 8·53 | 6·85 |
| $CO_2$ . . . . | 2·19 | 2·60 |
| Glycerol . . . . | 3·44 | 2·92 |
| $H_2O$ . . . . | 77·73 | 79·98 |
| | 100·00 | 100·00 |

There is here an indication that " substances other than anhydrous soap " are less concentrated in respect to water after treatment than before. This would appear to mean that the globules separating out consist of a more concentrated solution than the aqueous portion remaining in the soap.

This result might be expected if a portion of the water in the solid soap were combined as water of hydration and suggests therefore that even in the presence of highly concentrated electrolytes, soap fibres still retain some water of hydration.

McBain has shown that in the presence of nearly saturated salt solution, sodium. palmitate retains two molecules of water.

*Contribution from the Central Technical Department,*
*Messrs. Lever Brothers, Limited,*
*Port Sunlight.*

[4] *Colloid Chemistry,* chapter " Diffusion in Jellies," by Dr. Raphael Ed. Liesegang, Vol. I., 1928, edited by Jerome Alexander.

# EQUILIBRIUM BETWEEN MICELLES AND SIMPLE IONS, WITH PARTICULAR REFERENCE TO THE SOLUBILITY OF LONG-CHAIN SALTS.

By R. C. Murray and G. S. Hartley (*London*).

In 1927, Jones and Bury,[1] in discussing their freezing-point data for aqueous solutions of butyric acid, pointed out that these showed a sudden departure from the normal within a small range of concentration, and that this was a natural consequence of the law of mass action where micelles containing a considerable number of simple molecules were formed. Later, Grindley and Bury,[2] and Davies and Bury,[3] extended this principle to a study of the partial specific volumes of butyric acid and potassium octoate in aqueous solution and found that these properties also showed fairly abrupt changes in the neighbourhood of
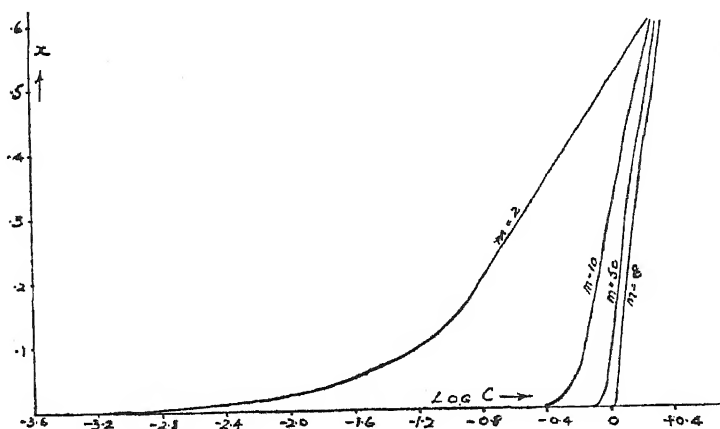


FIG. 1.

what they called the "critical concentration for micelles." This concentration for potassium octoate was in agreement with the evidence from the freezing-point data of McBain, Laing and Titley.[4]

The reason for this effect is that the concentration of micelles containing $m$ simple molecules will be proportional to the $m$th power of the simple molecule concentration, and therefore, once it has become an appreciable fraction of the whole, will commence to increase very rapidly if $m$ is large, as reference to the equations given later will make clear. In Fig. 1 the fraction of the solute existing in micellar form is

[1] Jones and Bury, *Phil. Mag.*, 4, 841, 1927.
[2] Grindley and Bury, *J. Chem. Soc.*, 679, 1929.
[3] Davies and Bury, *J. Chem. Soc.*, 2263, 1930.
[4] McBain, Laing and Titley, *J. Chem. Soc.*, 121, 622, 1922 ; see also Randall, McBain and White, *J. Am. Chem. Soc.*, 48, 2517, 1926.

plotted against the logarithm of the total concentration for values of $m$ of 2, 10, 50 and infinity. The effect of changing the equilibrium constant is merely to cause a parallel displacement of the curves along the log C scale. That the abruptness of the change increases with increasing $m$ will perhaps be made even more manifest if we give the ratios of the concentrations of solutions in which 50 per cent. and 1 per cent. respectively of the solute exists in aggregated form. For the values of $m$ chosen these ratios are 196, 3·30, 2·17, and 1·98. The value infinity for $m$ corresponds to the case where the solute is separating out as a second phase, and it will be seen that in this property, as in some others, the colloid takes an intermediate position between a one-phase and a two-phase system.

The change in the physical property-concentration curves would be expected to be even more abrupt in the higher long-chain salts than in the substances examined by Bury and collaborators, as they presumably form larger micelles. It is somewhat obscured, however, in the ordinary soaps by the fact that it occurs in very low concentrations where hydrolysis is a considerable complication, but Ekwall [5] has found that the equivalent conductivity of sodium myristate, which is largely due in very dilute solutions to hydroxyl ions and falls very rapidly with increasing concentration on account of diminishing hydrolysis, shows a short arrest at about 0·006 $N$ which is presumably due to micelle formation. In the solutions of the unhydrolysed long-chain salts, an abrupt change is very evident. Lottermoser and Püschel [6] find a sudden fall of equivalent conductivity in the case of the salts of the higher alkyl sulphuric acids, and similar behaviour in the case of cetyl sulphonates and cetyl pyridinium salts in the neighbourhood of $N/1000$ has been observed in this laboratory. Lottermoser and Püschel also find an abrupt change in the *surface tension* of the alkyl sulphate solutions at the same concentration, as that at which the conductivity change occurs.

It is well known [7] that the solubility of soaps is a rather peculiar function of temperature, systems of nearly any composition of soap and water becoming homogeneous at almost the same temperature, a fact which gives rise to the expression " melting-point of soap curds." Krafft [8] sought to relate this solution temperature to the melting-point of the fatty acid from which the soap is derived, in that the latter temperature is always slightly higher than the former, presumably having in mind that the underlying causes were similar. Reychler [9] suggested that the desolution phenomenon, a rapid crystallisation of the disperse phase over a range of about 1° C., was a solid-liquid transition and that solution was the reverse process. Solubility results for cetyl sulphonic acid and its alkali salts, obtained by observation of the clarification temperatures of mixtures of known composition on slow heating, and recorded in Fig. 2 do not lend support to this view, mainly because of the difference in solution temperatures of the various salts. Thus the sodium salt has its solution temperature 4° C. above the melting-point of cetyl sulphonic acid (54° C.), while the acid itself has its solution temperature 18° C. below. Any relation to the melting-points of the salts themselves is out of the question as these are all above 300° C.

[5] Ekwall, *Z. physikal. Chem.*, **161,** 195, 1932.

[6] Lottermoser and Püschel, *Koll. Z.*, **53,** 175, 1933.

[7] See, for instance, McBain, Lazarus and Pitter, *Z. physikal. Chem.*, **147,** 87, 1930.

[8] Krafft and Wiglow, *Ber.*, **28,** 2566, 1895.

[9] Reychler, *Kol. Zeit.*, **12,** 277, 1913.

"The melting-point of curds" phenomenon means that we have a sudden large increase of solubility over a very short range of temperature and it seems to us that this has in all probability a similar explanation to the other sudden transitions previously mentioned. If the concentration of the non-aggregated form in equilibrium with the solid increases steadily in the usual way with increasing temperature, then as, after a fairly definite critical concentration is reached, the ratio of micellar to non-micellar form increases very rapidly, we shall have the effect of a very rapid increase of total solubility with increasing temperature once a certain temperature is reached. This explanation, which is also suggested by Lottermoser and Püschel,[10] shifts the responsibility for the anomaly from the temperature to the concentration, the sharp rise of solubility occurring at a certain temperature only because it is at this temperature that a certain concentration is reached. It therefore offers at once an easy explanation of the solution temperatures
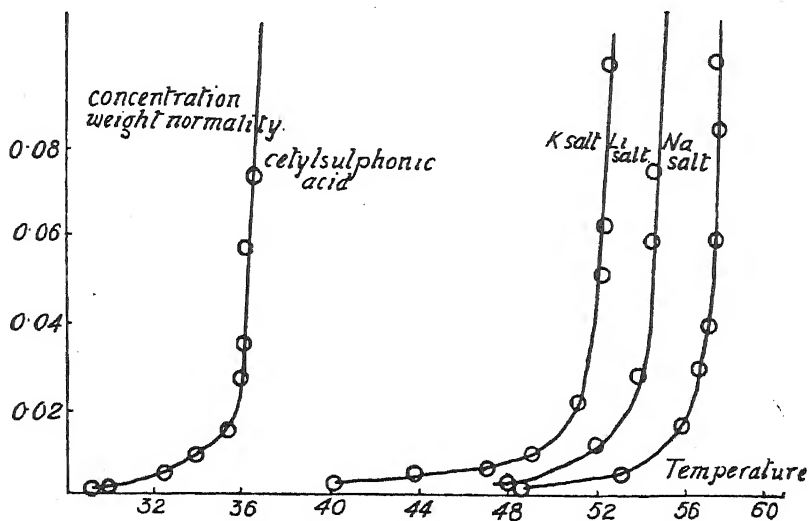


FIG. 2.

being different for different salts, this being simply due to their differences of "non-micellar" solubility.

We will consider first the case of an aggregating non-electrolyte. The solubility of an ideal solute will change with temperature according to an equation of the form

$$\log C = A + B/T \qquad . \qquad . \qquad . \qquad . \quad (1)$$

if its latent heat of fusion is independent of temperature, $C$ being the saturation concentration and $A$ and $B$ constants. Since we are concerned with small variations of temperature and with solutes whose behaviour will be far from ideal, we shall write this, with a sacrifice of formal exactness but a gain of convenience in the form

$$\log C = A + B \cdot T \qquad . \qquad . \qquad . \qquad . \quad (2)$$

In the case where aggregation occurs, we will assume that it is the concentration of simple molecules, $C(1 - x)$, which satisfies this equation,

[10] Reference 6, p. 179.

$x$ being the fraction of the solute in the aggregated state. We can obtain $x$ in terms of the total concentration from the mass action equation which becomes

$$K \cdot Cx/m = C^m(1-x)^m$$

$K$ being the dissociation constant of the micelle and $m$ the number of simple molecules in it. Converting this to the more convenient logarithmic form

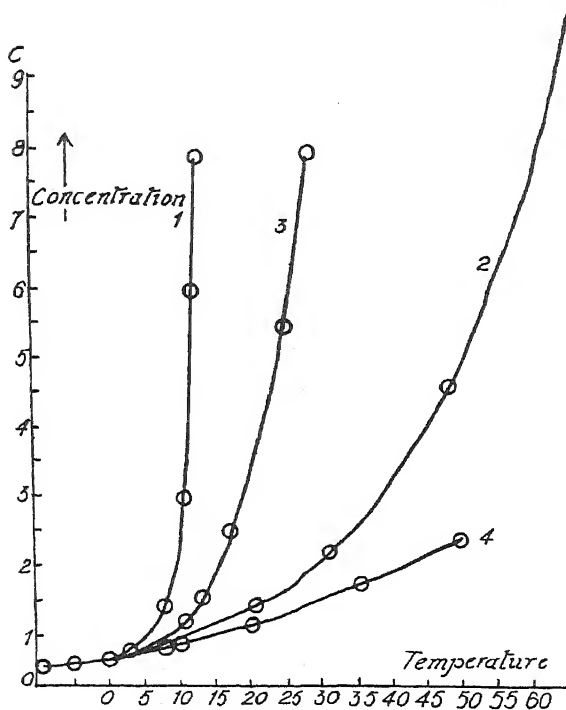$$(m-1) \cdot \log C = \log x - m \cdot \log(1-x) + \log K/m \qquad . \quad (3)$$

and taking an arbitrary value of 1 for $K$, values of $C$ corresponding to various values of $x$ have been calculated. In this manner the curves in Fig. 1, referred to above, were obtained.

Since we decided that $C$ in equation (2) should be taken as the concentration of simple molecules, the equation becomes

$$\log C + \log(1-x) = A + B \cdot T \quad . \quad (4)$$

With suitable values of $A$ and $B$, the corresponding values of $T$ were calculated and used in constructing curve No.



FIG. 3.

1 of Fig. 3, which represents the solubility of a non-electrolyte whose molecules aggregate into groups of 20, assuming a quite normal value (0·01) for $B$, the temperature coefficient of simple solubility.

Equations (3) and (4) may be rewritten

$$\overline{m-1}\left(\log C - \frac{\log K/m}{m-1}\right) = \log x - m(\log(1-x))$$

and

$$\left(\log C - \frac{\log K/m}{m-1}\right) + \log(1-x) = A + BT - \frac{\log K/m}{m-1}$$

from which it is apparent that a change in $K$ produces no change in the *form* of the curve (if the concentrations were measured in arbitrary units of $(K/m)^{1/m-1}$, the curves would be superimposable), but merely displaces the curve along the temperature axis just as would a change of $A$. The curve obtained (No. 1 of Fig. 3) is entirely different from

the curve (No. 4) for a non-aggregating substance having the same $A$ and $B$ values.

Comparison of curve I with the experimental curves (Fig. 2), however, shows that the change is far more abrupt in the former than in the latter, and comparison of the experimental curves for solubility with a typical experimental conductivity-concentration curve (potassium salt at 80° C. Fig. 4) shows that the solubility transition is very much less abrupt than that of the equivalent conductivity. An enormous change in the latter occurs between 0·0016 and 0·01 $N$, while the solubility does not rise very sharply till after the latter concentration is exceeded. The apparent discrepancy between the conductivity and the solubility transitions is easily explained if the modifications needed in the equations due to the fact that we are dealing with an electrolyte are considered.
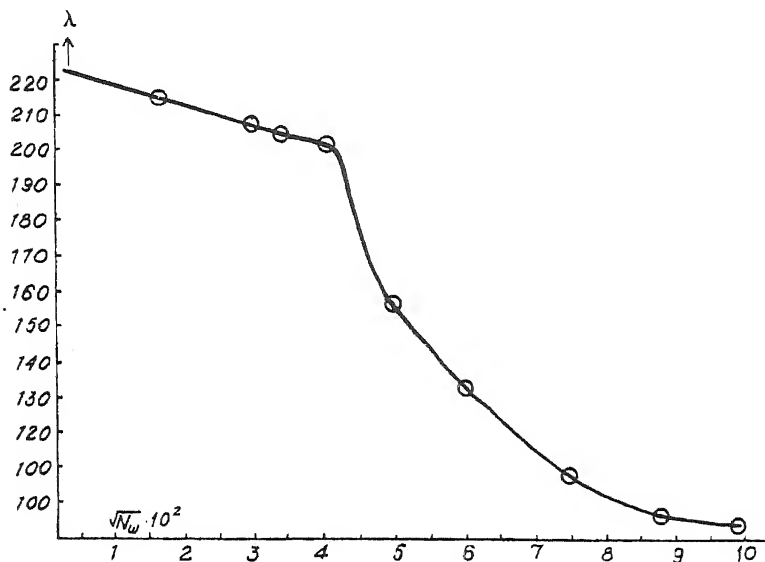


FIG. 4.

Consider first the case of a completely dissociated univalent electrolyte, ions of one kind and one kind only aggregating to form a micelle of twenty simple ions. The distribution equation (3) remains the same as before if we assume for the moment that the mass action law still holds, but we shall now have to insert for $C$ in the solubility equation (2) not the concentration of unaggregated ions of the aggregating kind, but the product of the concentrations of the two kinds of simple ions, i.e. not $C(\text{I} - x)$ but $C \cdot C(\text{I} - x)$. This equation therefore becomes

$$2 \log C + \log (\text{I} - x) = A + B \cdot T \quad . \quad . \quad . \quad (5)$$

From this equation and (3) curve 2 of Fig. 3 was constructed, the constants being chosen so that the initial portion of the curve coincided with that of I and 4. It is to be noted that it is much less sharp than the similar curve I for the non-ionic micelle case.

If we are dealing with ionic rather than molecular micelles, the gradualness of the solubility transition as compared with that of the conductivity is thus easily explained, but curve 2 shows perhaps an even

more gradual transition than is actually the case. It is improbable, however, that the micelles will contain no adherent gegenions, and that the mass action law can be assumed true for an ionic aggregation. The latter will be considerably modified by the changing influence of the ionic atmospheres and the number of gegenions adherent to the micelle will certainly increase with increasing concentration. An exact correction for both effects would be too complicated and uncertain in the present state of our knowledge to be worth the trouble of attempting, but we may get some idea as to the direction of the modification to which they would lead by considering separately two artificial cases—(a) the effect of the atmospheres alone assuming no adherent gegenions, and (b) the effect of assuming a definite number of gegenions, independent of concentration, to be included in each micelle and subject to a mass action law, the activity coefficients all being assumed unity.

The first of these calculations, based on the computations considered by one of us (G.S.H.) in another contribution to this discussion, show that the effect would be a considerable sharpening of the solubility curve, the atmosphere becoming closer with increasing concentration and thus facilitating the formation of the micelle by reducing the strong potential up which the single long-chain ions must travel if they are to aggregate. The second calculation is made by modifying the equations (3) and (5) in an obvious manner as follows, $n$ being the number of gegenions adherent to each micelle,

$$(m + n - 1) \log C = \log x - m \log (1 - x) - n \, \log \left( 1 - \frac{nx}{m} \right)$$
$$+ \log K/m \quad (6)$$

$$2 \log C + \log (1 - x) + \log \left( 1 - \frac{n}{m}x \right) = A + BT \quad . \quad (7)$$

A solubility curve for the case of $n = 10$, $A$, $B$ and $m$ being as before is shown in Fig. 3 (No. 3). It will be seen that the effect of adherent gegenions is to sharpen the curve. Since both these factors operate to bring the form of the ionic micelle curve closer to that of the non-ionic micelle curve, it may be assumed that the complicated combination of the two which will be in fact operative will also have this effect.

Preliminary determinations by a filtration technique of the solubility of the salts at lower temperatures show that these follow the same order as those at higher temperatures, thus indicating that the cause of the difference in the solution temperatures is to be sought not in a difference of the size of micelle formed or of its dissociation constant, but in the difference of the " non-micellar solubilities."

The rather unusual order in which the salts range themselves as regards increasing solubility, namely, Na, Li, K, is presumably due to the fact, found by analysis, that the lithium salt crystallises with one molecule of water.

The effect of the atmospheres and the adherent gegenions on the equilibrium between simple long-chain ions and micelles is of considerable interest. From equation (6) it was found that, with increasing total concentration, the single long-chain ion concentration actually rises to a maximum and then decreases, and a similar decrease can be predicted from consideration of the direct effect of the atmospheres. The transition from the simple to the aggregated form will therefore be even more sudden in the case of an electrolyte than in the case of a non-ionised substance. An interesting outcome of this property is that the

presence of a considerable concentration of a more soluble long-chain salt will actually increase the solubility of a less soluble one by removal of the simple long-chain ions supplied by the latter to form micelles. An experimental verification of this prediction was found in that cetyl sulphonic acid at a concentration of N/100 *decreased* by some 10° *C.* the solution temperature of the lithium salt, the latter being when dissolved at a concentration of N/300.

## Summary.

It is shown how the equilibrium between micelle and simple ions is capable of explaining the anomalous solubility-temperature curves of long-chain salts.

From the fact that the transition from a normal temperature coefficient to the extremely high one characteristic of the long-chain salts is not so abrupt as the sudden changes of the conductivity- and surface tension-concentration curves, it is concluded that the type of aggregation in dilute solution is predominantly ionic.

*Sir William Ramsay Laboratories of*
    *Inorganic and Physical Chemistry,*
        *University College, London.*

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# SOAP MICELLES.

By A. S. C. Lawrence, Ph.D.

The *micelle* is the kinetic unit of the disperse phase in colloidal solutions. It differs from the units in ordinary solutions—the molecule and the ion—in that it is much larger. For this reason, which is often intensified by non-spherical shape, it may not be completely free in its movements although free to thermodynamical tests. In some cases we know the micelle only as a statistical grouping of molecules, but sometimes we can learn something more than their average size; of their shape and of the manner in which they are built up from molecules. In these cases we can explain the bulk colloidal properties of the solution in terms of the objective micelles. The soaps provide a particularly good case for examination in this manner owing to the large amount of trustworthy information available from the well-known work of McBain and his co-workers; and also to the simplicity of the soap molecules, which are the starting-point of colloidal aggregation and, therefore, of our enquiry.

One difficulty appears at once. McBain remarks that the more soap solutions are studied the more crystalloidal they seem. Most of his measurements were made at 90° C., and, at this temperature, the sodium salts of even the higher fatty saturated acids do not display marked colloidal properties. This is because of the small size of the micelle. According to McBain's figures, the ionic micelle only contains some ten molecules; that is the micellar weight is 3000. Much larger micelles are required for the full development of those properties usually regarded as criteria of colloidal dispersion. However, at lower temperatures and in the more concentrated hot solutions all these properties are found.

McBain's data suggest that the size of the ionic micelle * does not
vary much with concentration.  But the neutral micelle is larger and
it is to this that the colloidal properties must be due.  These increase
with increase of concentration.  Is this due to the greater number of
particles present or is it due to increase of size ?  What are the factors
determining the size of the ionic micelle and that of the neutral micelle ?
    Restraint on the free motion of micelles is the origin of many of
the peculiar properties of colloids.  It is the reason why they cannot be
defined as homogeneous or non-homogeneous, one phase or two phase,
isotropic or anisotropic and so on unless the actual test used to designate
them is also stated.  Gels are isotropic optically, but obviously not so
mechanically; 1 per cent. ammonium oleate is a liquid with a viscosity only
slightly greater than that of water (except at very low rates of shear) but is
macroscopically elastic.  The electrical conductivity of some soap
solutions is the same whether in the form of sol or gel.[1]  This observation
has been described as meaning that gel and " fluid " sol have the same
conductivity.  But it does not mean that.  It means that the restriction
to movement of ionic micelles is the same in the sol as in the gel of the
same concentration.  The sol has anomalous viscosity.[2]  At low rates
of shear the apparent viscosity becomes very large.  The rate of shear
due to migration of an ionic micelle is small so that we must allow for
a viscous resistance which has no relation to the viscosity measured at
some arbitrary rate of shear.  Of course if the micelles are not free to
move individually, then they will move all together, neutral ones holding
ionised ones in a coherent structure.  Or, if the structure adheres to
the wall of the vessel used, then electro-osmose will occur.  Both of
these phenomena have been reported in soap solutions of sufficient
concentration to show structure.[3]
    Staudinger's method for calculating the concentration at which inter-
ference of anisodimensional micelles begins may be applied to soap
solutions.  The critical concentration of transition from sol-type solution
to gel-type solution is that at which the total effective volume of the
micelles is equal to the volume of the solution.  The effective volume
of the anisodimensional micelles is estimated as $\pi(l/2)^2\theta$ multiplied by
the number present.  $l$ is the length of the particle, and $\theta$ its thickness.
In several cases examined this transition, which shows itself as an in-
creased slope of the viscosity/concentration curve, is quite sharp.  As
the concentration increases further, there will be more and more inter-
penetration of the micelles until structure becomes evident in the solution
as anomalous flow.  That is, the Poiseuille equation no longer holds ;
the volume efflux is not proportional to the pressure head for small
pressures and at small rates of shear the apparent viscosity calculated
by mis-application of the Poiseuille equation increases to very large values.
At some concentration, gelation will occur but it is clear on this view
of the structure that there can be no sharp transition from sol to gel.
In any case the minimum amount of structure required for gelation
depends upon the value of the yield point required.  This is usually
taken arbitrarily as the force of gravity acting on the gel.  For any

    * In McBain's terminology, the ionic micelle is the highly mobile completely
dissociated group of about 10 molecules.  The neutral micelle is larger and
is not dissociated.  He considers that it has only a very small charge.
    [1] M. E. Laing and J. W. McBain, *J. Chem. Soc.*, 1506, 1920 ;  M. E. Laing,
*J. Physic. Chem.*, 673, 1924.
    [2] *Koll. Z.*, **13**, 88, 1913.                    [3] *J. Physic. Chem.*, 686, 1924.

chosen deforming force, the full gel structure will take a very long time to reach its full extent since by definition it is due to the clumsy aniso-dimensional micelles interfering with each other's movement. Development of maximum rigidity by random movements of the particles in a system equilibrating at a fixed temperature is retarded by the very factor to which the rigidity is due. Where gelation does occur reasonably suddenly, it is due to supersaturation and such gels are found to exhibit increase of rigidity over periods of weeks or months.[4] In more dilute solutions gelation may not occur for days or weeks.

Taking McBain's estimate for the size of the ionic micelle and assuming that the ten molecules are arranged side by side, $l$ becomes 50 Å.U. If then the length of the molecule is taken for $\theta$ (25 Å.U.), the effective volume, $n \, \pi(l/2)^2\theta$, allows us to calculate $n$, the number of particles per 100 c.c. and $n \times 10 \times 300/N = c$, where $c$ is critical concentration and $N$ Avogadro's number. This gives a critical concentration of 10 per cent. It is clear therefore that we need not consider seriously such small micelles and, conversely, that the observed structures require the presence of much larger micelles. The effective volume increases as the square of the length ; if, then, association is linear, the number of micelles required to reach the critical point falls off as the square of the number of molecules per micelle. But the mass concentration required to form a given number of micelles increases with the length of the micelle so that the net effect is that the critical concentration is a linear function of the association provided association is linear.

We cannot apply this simple picture of the structure in solutions to polydisperse systems, but it is certain that the structure of neutral micelles must affect the migration of ionic micelles either by preventing their passage or by adhering to them. From the published data it appears that free migration occurs in sodium oleate solutions when the concentration is below 0·3 per cent. Even where migration is unimpeded by structure, the anisodimensional form of the micelle must be considered. It has been pointed out that the mobility of an ionic micelle will be greater than that of the single ions since the charge increases with the number of molecules in the micelle (provided there is complete dissociation) while the viscous resistance increases as the square of the radius, which increases as the cube root of the number of molecules in the micelle. So that the viscous resistance increases as the $2/3$ power of the net charge. If, however, association is linear, the Stokes resistance is directly proportional to the number of molecules and therefore to the net charge. In absence of interference, therefore, mobility would be independent of the length of anisodimensional micelles.

## The Structure of the Micelles.

In addition to the problems of the size and structure of the ionic and neutral micelles, there are two changes in the structure of soap solutions which must be considered. First, the formation of " curd " of sodium soaps. This is a hard opaque white mass quite distinct from the soft more transparent intermediate form exemplified by the potassium soaps. The second is the *Krafft point*.[5] This is a temperature range of a few degrees over which the solubility increases very rapidly. So much so that it has been incorrectly described as a melting of the curd soap.

[4] Hatschek, *Trans. Faraday Soc.*, 1108, 1933.
[5] Krafft and Wiglow, *Ber.*, **28**, 2566, 1895.

This is incorrect because the Krafft transition and the curding transition are distinct and, as will be suggested in the following pages, of a different nature.

## The Ionic Micelle.

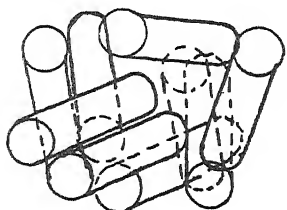It is necessary to insist that the primary cause of colloidal aggregation is insolubility.   The soap molecule contains a polar group which cannot carry the whole molecule into molecular dispersion.   There is a part of the hydrocarbon chain which is not wetted.   From the experimental fact that colloid particles are first detected in the homologous series of fatty acids at the $C_6$ member,[6] we may assume that any further lengthening of the molecule involves increase of the water-insoluble part with consequent increase of interfacial surface.   The free interfacial energy is reduced by aggregation of the molecules in such manner that the hydrocarbon chains lie alongside of one another to form a micelle whose exterior is hydrophilic.   Fig. 1 shows this diagramatically.   Actually the polar groups will be distributed over the whole surface and the volume of the particle is not much different from that of a sphere of which the diameter is the molecular length. This micelle penetrates ultra-filters with ease.[7]



FIG. 1.

The size of such a micelle depends   only upon the balance between the two parts of the heteropolar molecule.   Change of concentration will not affect the size of the micelle.

## The Neutral or Secondary Micelle.

The neutral micelle, so-called to distinguish it from the completely dissociated ionic micelle, has a small charge.   It travels to the anode and carries some sodium with it except in the most dilute solutions. If this were carried mechanically as a result of interference of neutral and ionic micelles,      these



FIG. 2.

would need to be very large.   For $N/100$ sodium oleate, the minimum micellar length would need, by Staudinger's method of calculation, to be 1700 Å.U.   There is no indication of such structure and it seems probable that the sodium is part of the micelle.
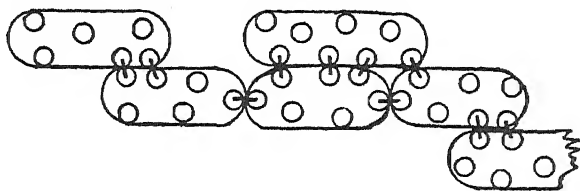
This micelle is secondary in that its formation involves more than simple colloidal aggregation.   It is suggested here that it is built up from primary ionic micelles or from molecules by a crystalloidal association at the polar groups, which is thus additive to the true colloidal aggregation.   The extent of dissociation will be determined in accordance

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[6] *Comptes Rendus.*, **146,** 484, 1908.
[7] J. W. McBain, and W. J. Jenkins, *J. Chem. Soc.*, 2325, 1922.

with the Mass Action Law. Undissociated micelles will aggregate to the larger secondary ones as the concentration increases but these will be stable micelles since they have a hydrophilic exterior. That this growth of secondary micelles is to some extent an increase of length is shown by the increase of viscosity. If they thickened without lengthening the viscosity would not rise. It does, however, rise rapidly with increase of concentration. Fig. 2 shows how a lengthening is to be expected. At any time a few of the exterior polar groups on the secondary micelles will be ionised so that they will migrate slowly to the anode carrying a large number of bound sodium atoms.

## Phase Changes in the Micelles.

(*a*) **The Krafft Point.**—On the picture given, the size of the secondary micelles continues to rise with increasing concentration or on cooling and there seems to be no reason why this process should not go on indefinitely. The optical properties and, less definitely, the viscosity show that this process does take place but another factor intervenes and alters the conditions upon which the extent of dispersion depends—the Krafft point. Krafft himself regarded the transition as a melting of the curd to form the much more highly dispersed and much more concentrated sol. The two processes are distinct, and, in some cases can be separated easily. In potassium soaps the sudden increase of dispersion occurs but without curd ever existing. Krafft pointed out that this temperature of sudden increase of dispersion of any sodium soap was in the neighbourhood of the melting-point of the fatty acid. This coincidence applies, not only to the saturated fatty acids but also the unsaturated oleic and erucic and to their geometrical isomers elaidic and brassidic. There seems no direct reason why there should be this coincidence since the polar groups are different in soap and free acid, but I have pointed out already that there is also a close correspondence between the fatty acids and the hydrocarbons containing twice as many carbon atoms as there are in the hydrocarbon chain of the fatty acid.[8] That is, between acids $C_nH_{2n+2}COOH$ and hydrocarbons $C_{2n}H_{4n+2}$. The reason for this agreement being that melting of the fatty acids does not involve rupture of the binary association of the carboxyl groups and suggests that lateral adhesion of the carboxyl groups is not a serious factor at the melting-point. The number of polymorphs and mesomorphs found in long chain compounds shows the need for considering the phase change from solid to liquid as a process of steps occurring at different temperatures, so that the so-called melting-point may involve the appearance of only one extra degree of freedom.[9] If this view is applied to the soap micelles, then Krafft's observation means that in the micelles undergoing this transformation, the molecules are associated in pairs by their —COONa groups. This confirms the assumption made concerning the nature of the secondary micelle. The Krafft transition is then due to the loosening of the attractive forces between hydrocarbon chains throughout the micelle. This is a phase change of their adhesion; from solid to liquid. The degree of dispersion is thereby greatly increased. With the increase of free —COONa groups the number of

[8] *Koll. Z.*, **50**, 12, 1930.
[9] Friedel, *Ann. Physique*, **18**, 271, 1922.
[10] A. S. C. Lawrence, *Trans. Faraday Soc.*, **29**, 1008, 1933 ; *Science Progress*, Oct., 339, 1933.
[11] P. A. Thiessen and E. Ehrlich, *Z. physik. Chem.*, 299B, 1932.

ionised micelles will also increase in accordance with the Mass Action Law.

## Phase Changes in the Micelles.

(b) **Curd.**—Curding is a recrystallisation in the micelles. The term "curd fibre" is used vaguely and is objectionable since the fibrous shape is merely pseudomorphic of the fibrils of the phase from which the curd formed. The nature of this phase is unfortunately obscure owing to the confusion about the nature of the solid and semi-solid forms of soap/water systems. The possibility of correlating scattered published observations is remote since some are demonstrably incorrect and in others the nature of the system under examination is not defined. Nor can meaning be attached to X-ray examination since the detection of a regular periodicity gives no clue to which unit in the system is built up with that regularity nor of its size, or shape.
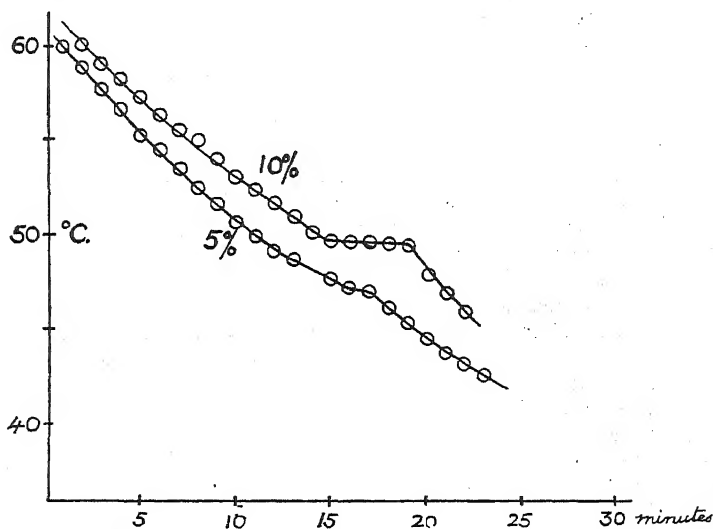


FIG. 3.—Cooling curves of sodium stearate solutions.

Curding can be made to occur in solutions of potassium soaps by addition of potassium chloride. In absence of added salt potassium stearate forms semi-opaque very viscous liquids. In higher concentrations they may have a small plasticity but a 10 per cent. solution flows and shows optical streaming effects due to fibrils. When potassium chloride is present the streaming effects are much more distinct and the system is opaque and white and the viscosity appears to be somewhat smaller. Under the microscope, bright fibrils are seen between crossed nicols but these are not single fibrils as they seem and, if rubbed under a coverglass are separated into units not resolvable. Preliminary X-ray examination of the two forms (kindly made for me by Miss H. Megaw) proves that the structure has altered in the curding.

McBain has shown that in sodium laurate and sodium palmitate there is no change of osmotic activity at the curd change, thus proving that curding does not alter the degree of dispersion of the soap.[12]

[12] McBain and Salmon, *J. Chem. Soc.*, 1381, 1921.

Further proof of the phase change is provided by cooling curves of solutions of sodium stearate. Fig. 3 shows the results for 5 and 10 per cent. solutions in which there is clearly a phase change. In this case, it is very close to the Krafft transition but the two can be separated in another way. A solution of 10 per cent. of sodium oleate and 10 per cent. of sodium stearate shows the Krafft change and on cooling becomes a thick plastic paste but no curding takes place down to room temperature. On the picture of Fig. 2 curding as a recrystallisation would yield a microcrystalline curd owing to the small number of adjacent —COOHa groups having a common orientation. This would account for the marked opacity of curd.

There are sometimes indications that the curd form is a lamellar form. Photographs have been published of sodium laurate in this form and it is certain that all hot soap solutions deposit a very small amount of rhombic plates on cooling quickly. These are probably deposited from molecular dispersion. Soaps, by which I mean wet alkali salts of the fatty acids, are subject to this tendency to form fibrils. It is the cause of the high viscosities observed, which in the more concentrated systems are as great as $10^6$ absolute units.[13] This fibrillar growth is incompatible with the smectic state and it is very doubtful whether smectic soap/water systems exist. Photographs published as smectic focal conic structure are spherulitic fibrillar crystallisation and not the focal conic structure of Dupin's cyclides which distinguishes the smectic layer structure.

(*Laboratory of Colloid Science,*
 *Cambridge.*)

## GENERAL DISCUSSION.*

**Dr. C. R. Bury** (*Aberystwyth*) said : There is one complication which Murray and Hartley have not taken into account ; *i.e.*, that the number of simple ions in a micelle may not be constant. If the micelles were spherical, the number of simple ions in them would be determined by the dimensions of the simple ion and by geometrical considerations, and would not vary greatly from micelle to micelle, or on varying temperature or concentration. It is improbable, however, from the dimensions of the simple ions, and from some of the properties of concentrated soap solutions, that the micelles are spherical, and I think it probable that the number of simple ions in a micelle vary over a wide range, and is very susceptible to changes of temperature and concentration. Any treatment of soap solutions which assumes the number of simple ions in a micelle to be constant can only be regarded as a very rough approximation.

**Professor W. E. Garner** (*Bristol*) said : It is possible that the change in solubility referred to in the paper of Murray and Hartley is due to a change occurring in the solid state. Dr. Piper has recently shown that potassium palmitate undergoes a phase change at about 45° C.

**Dr. C. R. Bury** (*Aberystwyth*) said : An abrupt change in the slope of the solubility curves of soaps implies an abrupt change in the nature of the solid soap or in that of the solution in equilibrium

[13] McBain and Watts, *J. Rheology*, 437, 1932.
* On the two preceding papers.

with it.    Professor Garner suggests a change in the nature of the solid
is the cause of the abrupt change in the slope of the solubility curve.
But there are abrupt changes in the nature of the solution which
can account for the phenomenon.    With potassium octoate this abrupt
change in the properties of the solution has been correlated with the
abrupt change in the freezing-point curve, which is, of course, thermo-
dynamically equivalent to a solubility curve.[1]

**Dr. A. S. C. Lawrence** (*Cambridge*) said : Dr. Bury's results quoted
by him provide evidence of the dual nature of aggregation to micelles in
all but dilute sols.    In potassium octoate solutions there is discontinuity
additional to the change of slope due to primary micelle formation
which alone occurs in solutions of a fatty acid.    The discontinuity
must therefore represent the formation of secondary micelles and not
primary ones which are the only species considered by him.

**Mr. G. S. Hartley** (*London*) pointed out that two radically different
explanations of the Krafft point (clarification of a soap-water mixture
during a very small increase of temperature) had been put forward.
Dr. Lawrence considered that the phenomenon was caused by a
change in the rigidity of the crystalline soap phase at this tempera-
ture, while Mr. Murray and the speaker, following the line of argu-
ment of Bury, attributed it to a change in the constitution of the
*solution* within a small range of *concentration* and hence, incidentally,
within a small range of temperature.    The type of change of structure
considered probable by Dr. Lawrence was a loosening of the paraffin
part of the lattice (*i.e.* decrease in lateral adhesion of the long chains).
As Dr. Lawrence himself had emphasised, however, the long chains
can only be carried into solution by the water-soluble ionic " head,"
and it seemed to the speaker that a loosening of the paraffin part of the
structure would not therefore be expected greatly to facilitate dis-
solution in water, this requiring rather a loosening of the ionic lattice
permitting the attack of the ionic " heads " by the water, or, as Mr.
Murray and the speaker considered, a greatly increased solvent power
of the solution.    The great difference of the melting-points of the salts
and free acids showed that the ionic lattice was a much more stable
structure than the paraffin lattice and the speaker therefore considered
the explanation in terms of a change from single ions to micelles in
the solution more probable.    The fact that the Krafft temperatures
for different salts of the same acid were different seemed also difficult
to reconcile with the phase-change theory, the correspondence between
the melting-point of the acid and the Krafft point of the salts not being
a general phenomenon and therefore probably a coincidence.

**Dr. A. S. C. Lawrence** (*Cambridge*) said that he accepted Dr.
Hartley's view that a phase change of the hydrocarbon adhesion in soap
micelles was not alone sufficient to explain the large increase of solu-
bility over a small temperature range, which is conveniently known as
the Krafft point.[2]    He still claimed, however, that the considerations
developed by Hartley and Murray should be applied, not, as they had,
to a normal temperature solubility curve, but to the abnormal one
postulated in his paper.    And that the molecular solubility was affected
by the physical state of the non-polar part of the heteropolar molecules.
The nearest case is the greater solubility of an allotrope of higher osmotic

[1] Bury and Davies, *J.C.S.*, 2413, 1932 ; Davies, *J.C.S.*, 551, 1933.
[2] See p. 193 for distinction between this change and " curdling " which were
considered by Krafft as a single phenomenon.

pressure. Phase changes in monomolecular layers of myristic acid are accompanied by changes in the bulk solubility of the acid.[3]

Mr. Hartley's suggestion that the high melting-points of the soaps due to their ionic linkages show this to be a more stable binding than the hydrocarbon chain adhesion, has no bearing upon soap/water systems owing to hydration of the polar groups, whose adhesion is thereby greatly reduced. Sodium acetate, in the anhydrous state melts at 319° but, when hydrated with 3 molecules of water, melts at 58°. The hydration of the polar groups in soap/water systems is greater than this. McBain suggests about 12 molecules and I find that 6 are still held tenaciously at 200°.

In heteropolar substances of the type $\left(\text{P} \underline{\hspace{2cm}} \text{N}\right)$, the action of the two parts of the molecule is antagonistic. In a polar solvent, the non-polar part (N) is indifferent to the solvent, except to the limited extent to which the polar part can carry the molecule as a whole into true solution. Hence, by definition, colloids of this type must show phenomena due to the independent properties of the two parts. Colloidal properties are also observed in non-polar solvents, but in this case aggregation to micelles is by the polar groups and it is only the hydrocarbon chains that are separated by the solvent. It has no effect upon the adhesion of the polar groups and the system must be heated nearly to the melting-point (of the ionic lattice) before dispersion occurs. Hence sodium soaps show a " Krafft point " in paraffin at about 190°.[4] No heteropolar molecule is ideal since the influence of the polar group extends along the hydrocarbon chain ; in the sodium soaps, to the fifth or sixth carbon atom. The extent of this influence depends, of course, upon the nature of the polar group so that a very soluble one will lower the Krafft point further below the melting-point of the fatty acid present than will a less soluble one.

There is abundant though still somewhat esoteric evidence of transitions where a change of state occurs, not in the conventional way of a simultaneous phase change in which all the degrees of freedom participate, but by their step-by-step appearance. The most definite examples of this are long-chain heteropolar molecules.[5]

**Dr. A. Wassermann** (*London*) said : In connection with the anomalous solubilities of long-chain salts I would like to mention the ξ-tri-

methylpentadecabetain $(\text{Me})_3\overset{+}{\text{N}} \ldots (\text{CH}_2)_{14} \ldots \overset{\displaystyle /\!\!/^O}{\text{C}-\text{O}}^-$ synthesised by Kuhn and Giral.[6] This interesting compound is a long dipole. No attraction of the oppositely charged ends of the chain occurs. Owing to the large number of $CH_2$-groups one would expect small solubility in water. In fact, the dried substance is hygroscopic. Such long dipoles are of considerable interest for the theory of micellar formation.

**Mr. C. F. Goodeve** (*London*) said : While agreeing with Murray and Hartley that the experimental evidence described and referred to here, can most easily be explained by a dynamic equilibrium between the monomer (single molecule) and the micelle, the picture may be

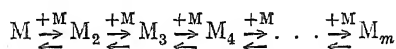[3] N. H. W. Addink, *J. Chem. Physics,* **2 (9)**, 575, 1934.

[4] Unpublished observations of the writer.

[5] See Faraday Society conference on Liquid Crystals and Anisotropic Melts, 1933, and P. A. Thiessen and E. Ehrlich, *Z. physik. Chem.,* **19**, 299, 135; **165A**, 453, 463, 1933.

[6] *Ber.,* **67**, 1130, 1934.

further elaborated from a kinetic point of view. It would appear that a substance such as a cetyl sulphonate salt, existing almost entirely as the monomer in dilute solutions, and forming micelles of say about 20 molecules in concentrated solutions, must pass through all the intermediate stages of association. The formation of the micelle from the monomer in one stage is, of course, highly improbable as it requires a collision of 20 molecules at one time. Furthermore, collisions between two intermediate aggregates leading to the micelle can only occur infrequently owing to their slower movement and the strong repulsion between their electric charges. The most frequent collisions will undoubtedly be between two molecules of the monomer or between one uncharged (unionised) monomer and an intermediate complex (mostly charged). Dissociation may take place by the removal of either an ionised or an unionised molecule.

From this point of view the equilibriums can be represented by :

$$M \underset{\leftarrow}{\overset{+M}{\rightleftharpoons}} M_2 \underset{\leftarrow}{\overset{+M}{\rightleftharpoons}} M_3 \underset{\leftarrow}{\overset{+M}{\rightleftharpoons}} M_4 \underset{\leftarrow}{\overset{+M}{\rightleftharpoons}} \ldots \underset{\leftarrow}{\overset{+M}{\rightleftharpoons}} M_m$$

where M represents the monomer molecules and $M_2$, $M_3$, etc. represent the corresponding aggregates.

The equilibrium concentrations of each of the intermediate aggregates will depend, (1) on the collision frequency constants for both association (bimolecular) and dissociation (unimolecular), (2) the energy of activation of the bimolecular association, and (3) the energy required to dissociate one monomer molecule from the aggregate. There is no apparent reason why the usual collision formula should not apply at least in a rough way and no great difference in the constants is to be expected. If the aggregates are held together by van der Waal's and not chemical forces, it is unlikely that an energy of activation must be overcome before association. It is therefore to be concluded that the controlling factor in determining the equilibrium concentrations of the intermediate aggregates is the third one above. A low concentration of these aggregates compared to that of the monomer and the micelles would indicate that the energy required increases with the state of aggregation and passes through a maximum corresponding to the micellar state.

The increase is to be expected from the accumulative mutual attraction between the molecules, and probably occurs in all types of precipitation. The decrease in the heat of association above the micellar stage is the special characteristic of these colloids and prevents the growth of the micelles to large flocculating particles. In the case of spherical particles it may mean that the outer lyophilic layer of the particle is now complete and has little or no attraction for the monomer molecule.

An indication of the amount of a colloid existing in an intermediate stage might be obtained from a study of the velocity with which equilibrium is set up. A high velocity, depending on collisions as described above, could only be obtained in the presence of an appreciable concentration of the intermediate aggregates.

**Mr. G. S. Hartley** (*London*) said : I am substantially in agreement with Mr. Goodeve's kinetic analysis. Undoubtedly the third factor enumerated by him is the most important, and in connection with it I should like to emphasise that one must consider chiefly the attraction between water molecules rather than between paraffin chains. The

latter aggregate not because they attract one another peculiarly strongly or more strongly than they attract water molecules but because the attraction between water molecules is far stronger than that between either of the other combinations. In the active sense it is the water molecules which aggregate, the paraffin chains being squeezed out into groups in consequence. A complete micelle will offer no paraffin surface to the water but only an ionic surface. Only a few ions may have to be removed to increase the paraffin/water surface enormously, while further removal would increase it but little, and consequently far more energy will be needed to remove an ion from a complete micelle than from an intermediate aggregate. Beyond a certain size, however, it may require considerable energy to *introduce* a further ion *into* the micelle because this would require deformation of the micelle or submergence of an ionic " head " into the paraffin interior, the outer hydrophylic layer being, as Mr. Goodeve says, complete.

**Dr. A. S. C. Lawrence** (*Cambridge*) said : Dr. Goodeve's remarks are very interesting since all workers on soap solutions are aware of marked " ageing " effects although the mechanism of the change has not hitherto received attention. The process is very slow which indicates, as Dr. Goodeve points out, that the concentration of the intermediate aggregates is small.

It might be suggested that there is a Maxwell distribution among the micelles so that the number, $n_1$, whose energy is above a critical level, E, is given by the usual equation :

$$\frac{n_1 m}{nm} = e^{-E/RT},$$

from which $E$ could be calculated where $n$ is the total number of micelles in the solution and $m$ is the number of molecules per micelle.

Such a view does not, however, take us very far owing to the formation of secondary micelles, the formation of which I have discussed in my paper. This secondary aggregation affects Dr. Goodeve's suggestions since the clearing at the Krafft point presupposes the presence of micelles very much larger than those suggested by him. These secondary micelles are built up by aggregation of the — COONa groups so that hindrance due to electrical repulsion does not affect this part of the " ageing."

**Mr. G. S. Hartley** (*London*) (*communicated*) : In regard to Dr. Lawrence's reference to slow ageing in soap solutions, I should like to point out that in the dilute solutions ($N/10$ and below) of many unhydrolysed long-chain salts investigated in this laboratory we have not detected any ageing effects. The formation of what Dr. Lawrence calls " primary " micelles is accompanied by a colour change of suitable indicators, equivalent to a change of nearly 2 $p_H$ units in some cases. On diluting a buffered solution of methyl red containing cetyl pyridinium chloride in concentration just above the micellar limit, a change from yellow to red is at once observed. I have been unable in any ordinary manipulation to detect any lag whatever in this change. If ageing occurs in *dilute* solutions of soaps, is it perhaps due to slow precipitation of acid soap ?

**Mr. R. C. Murray** (*London*) said : A loosening of the hydrocarbon chains in the solid phase is one which is dependent on temperature and closeness of packing of the chains in the lattice alone, and would not be expected to be influenced in any way by the presence of simple ions

in the water with which the solid is in contact. Thus we should not expect, on Dr. Lawrence's view of the cause of the sudden large increase of solubility of long-chain electrolytes, that the form and position of the solubility curve of say, potassium cetylsulphonate would be affected by the presence of such a salt as KCl in the aqueous phase, whereas, if the matter be viewed from the standpoint of the Law of Mass-action, it can easily be shown that a very considerable flattening out of the solubility curve is to be expected, if the quantity of KCl in the aqueous phase be adjusted so that, when the systems are homogeneous, the ratio (equivalents of KCl/equivalents of K cetylsulphonate) is constant. Experimentally it has been found that the solubility of potassium cetylsulphonate is very considerably flattened out under these circumstances, as the following figures, for the case in which the above mentioned ratio was made 10·8, show :—

| Concn. with respect to K Cetylsulphonate. | Solution Temperature. | |
|---|---|---|
| | Without KCl. | With KCl. |
| $N/10$ . . . | 52·3° C. | 72° C. |
| $N/50$ . . . | 51·2° C. | 60° C. |
| Difference . . | 1·1° C. | 12° C. |

The difference between the solution temperatures of the K, Li and Na cetylsulphonates is not very great, and it might be thought suggestive that they are so near together, and to the m.p. of the cetylsulphonic acid. Two salts have been found recently to have their solutions much more widely spaced apart ; these are the thallous, with the point at 65° C., and the silver, with its solution temperature at 135° C., — 80° C. above the m.p. of cetylsulphonic acid. It is very hard to understand how, if extensive solution is the natural consequence of the loosening of the hydrocarbon chains, the presence of silver ions in the lattice should delay it by as much as 80° C.

# THE INFLUENCE OF ATMOSPHERIC CARBONIC ACID UPON THE SURFACE TENSION OF AQUEOUS SOLUTIONS OF SODIUM SALTS OF FATTY ACIDS.

By A. Lottermoser, *Dresden.*

(*Experimental work by* B. Baumguertel.)

The influence of atmospheric carbon dioxide upon the surface tension of soap solutions is often mentioned in the literature. Preliminary experiments with sodium laurate solutions have shown that carbonic acid, by altering the hydrolytic equilibrium, influences the surface tension of these solutions very materially. We have, therefore, studied,
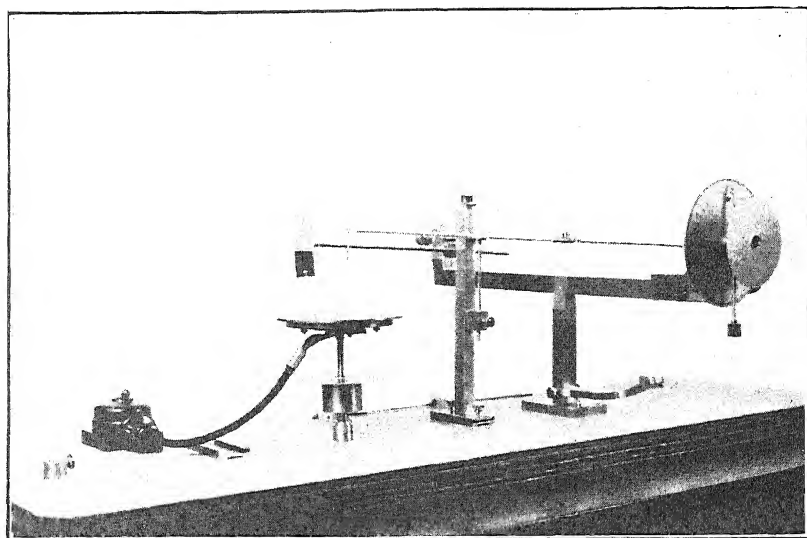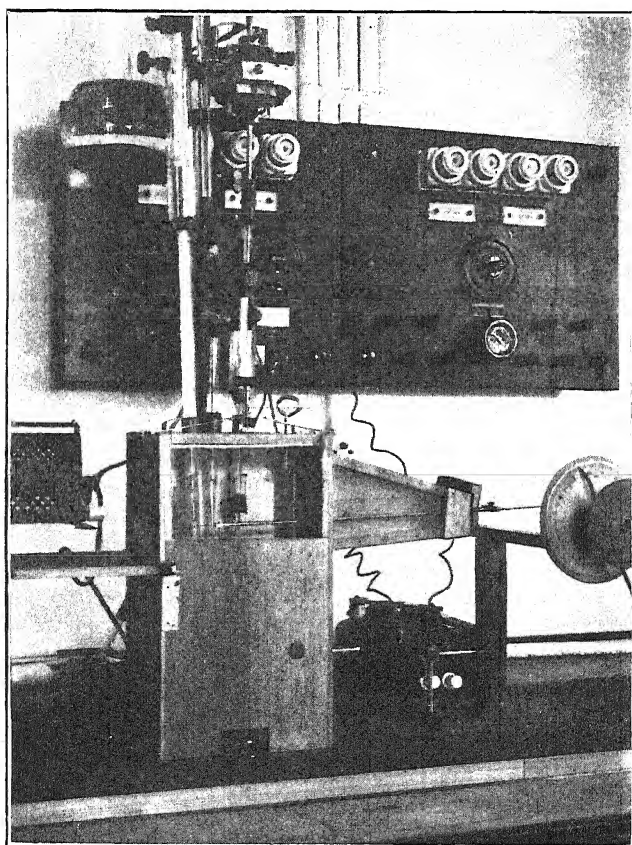
Fig. 1.



Fig. 2.

as set out below, this influence on numerous sodium salts of the homo-
logous series of alkylmonocarbonic acids and also on some compounds
similar to soaps. These investigations were carried out with a torsion
balance, constructed at the Institute of Colloid Chemistry at Dresden,
which is based essentially upon the principle of *Lecomte du Nouy* [1] and
is reproduced in Fig. 1. This method of measurement allows at the same
time the determination of changes in the adsorption equilibrium, *i.e.*,
the velocity with which the static surface tension follows changes in the
conditions. We are therefore in a position to report upon the velocity
of decrease of surface tension in soap solutions, which have often been
the subject of discussion.

In order to be able to carry out the surface tension measurements
under conditions in which carbon dioxide is excluded, we built a box
in which one half of the balance arm with the pull-off ring and the soap
solution to be tested could be maintained under air-tight conditions
(*cf.* Fig. 2). During the measurement of the surface tension of the soap
solutions with exclusion of carbonic acid a current of air free from dioxide
was led through the box.

The solutions were prepared by the saponification of carefully weighed
quantities of fatty acids of the greatest purity, with equivalent parts of
$N/2$ NaOH free from carbonate, in water free from dioxide, under a reflux
condenser. During saponification a current of air, free from $CO_2$, was
led through the saponification flask, so as to prevent any back flow of
$CO_2$ into the flask through the reflux cooler. The dilute soap solutions
were not prepared by diluting the concentrated ones but, for every con-
centration fresh solutions were made, in order to avoid any influence due
to ageing.

The influence of atmospheric $CO_2$ upon the surface tension was prelimi-
narily tested with aqueous solutions of different concentration of the
following sodium salts: formate, acetate, butyrate, capronate, caprylate,
caprinate, laurinate, myristate, palmitate, stearate, in the following
manner: the freshly made solutions, after cooling, were tested at once in
the $CO_2$-free box for surface tension and then allowed to age under ex-
clusion of $CO_2$ for one hour, their surface tension being measured repeatedly
during this time. The ageing effect resulting under these conditions is in the
following paragraph called (" Ageing period I "). After this, the $CO_2$-free air
current was stopped, so that air containing $CO_2$ could enter through a small
slit—where the balance-arm enters the box too. In this condition measure-
ments were repeatedly made during half an hour (" Ageing period II ").
Finally the box was opened so that the air could act freely upon the solu-
tion under examination. Under these conditions the measurements were
continued during several hours or days (" Ageing period III "). In addition
to this, a part of each solution was kept in an Erlenmeyer flask for twenty
hours under exclusion of $CO_2$ and then its surface tension was measured
again under exclusion of $CO_2$ (" Ageing period IV "). All the measurements
were made at room temperature, which varied only slightly round about
$20°$ C., with the exception of some higher concentrated sodium myristate and
palmitate solutions, which had to be tested at higher temperatures, because
of their gelatination at room temperature.—It should be said from the
beginning that all these measurements are of a semi-quantitative nature,
because the quantity of $CO_2$ has not been taken into consideration. How-
ever, we have always experimented under exactly the same conditions, so
that one is well justified in making comparisons as to the influence of
$CO_2$ upon the surface tension of the solutions of the various salts as well
as to their different concentrations.

The result of these measurements was that, with exclusion of $CO_2$

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[1] P. Lecomte du Nouy: *Biochem. Z.*, 115, 113 (1925).

the surface tension remains constant, no matter how long the time during which the tests may be continued, whilst with access of air containing $CO_2$ the tension reaches a minimum, partly after some hours, partly after several days, and then rises slowly again. The influence of $CO_2$ rises as the number of carbon atoms of the fatty acids increases, a circumstance which is caused by the diminishing strength of the acids set free by the $CO_2$. The difference is small from sodium formate up to the caprylate reaches its peak with the myristate and falls off again with the palmitate. This latter fact, as well as the renewed increase in the surface tension is due to a turbidity or even a precipitate, which is formed with prolonged action of $CO_2$ and which is followed by a diminution of the concentration and thereby an increase of the surface tension. This happens with the stearate and palmitate at such an early stage that it counteracts the diminution of the surface tension by $CO_2$.

Furthermore the influence of salt concentration upon the diminution of the surface tension by $CO_2$ has been investigated. It was found that the influence of $CO_2$ increases with the salt concentration when low molecular salt solutions are used, whilst it diminishes with rising concentration of the typical soap solutions. We had expected typical soap solutions to behave in this way since hydrolysis increases with dilution, but we cannot give a satisfactory explanation of the behaviour of the salts of low molecular weight.

In almost all references in the literature up to date the surface tension of soap solutions is given without regard to the influence of $CO_2$. This fact has induced us to make new measurements under conditions of exclusion of $CO_2$, in order to determine their dependency upon temperature and concentration.

**Temperature Influence.**—We have been able to ascertain that the surface tension quite generally diminishes along a straight line with the temperature, so long as clear solutions are present. This phenomenon can be expressed by the following formula :

$$\sigma = \sigma_c \left(1 + R[t_c - t]\right).$$

The temperature coefficient becomes the smaller,
(1) the higher molecular the fatty acid,
(2) the higher the salt concentration.
Sodium formate is the only salt which shows a rising temperature coefficient with rising concentration.

**Influence of Salt Concentration.**—The results of these experiments are illustrated by Fig. 3, which shows that within a certain limit of concentration the surface tension falls off in a straight line with the logarithm of concentration. This can be formulated by the following equation :

$$\sigma_{c'} = \sigma_c \left(1 + R[\log c - \log c']\right).$$

The concentration at which this steep falling-off begins becomes smaller and smaller with increasing number of C-atoms of the fatty acid. The higher the molecular weight of the fatty acid, the steeper is the decline. In high concentrations, simultaneously with incipient turbidity, the curve reverts. Sodium formate has no capillary activity, it even raises the surface tension in high concentration. The salts from sodium acetate up to the caprylate have only small capillary activity, whilst the typical soap character begins with the caprinate.

**The Surface Tension of Sodium Oleate Solutions.**—The same experiments as made with the salts of the saturated fatty acids were carried out with sodium oleate. Having regard to the well-known sensi-

tivity of the oleic acid to oxygen, the experiments were made in a current of nitrogen free from $CO_2$ and $O_2$, since we have stated that the atmospheric oxygen modifies the surface tension of an oleate solution, especially in dilute solutions. The alteration is small but it can be measured. We have ascertained that the surface tension remains constant with the time, when $CO_2$ is excluded, and that the action of $CO_2$ is stronger in dilute solutions than in concentrated ones. With rising temperature the tension falls again in a straight line, but the temperature coefficient
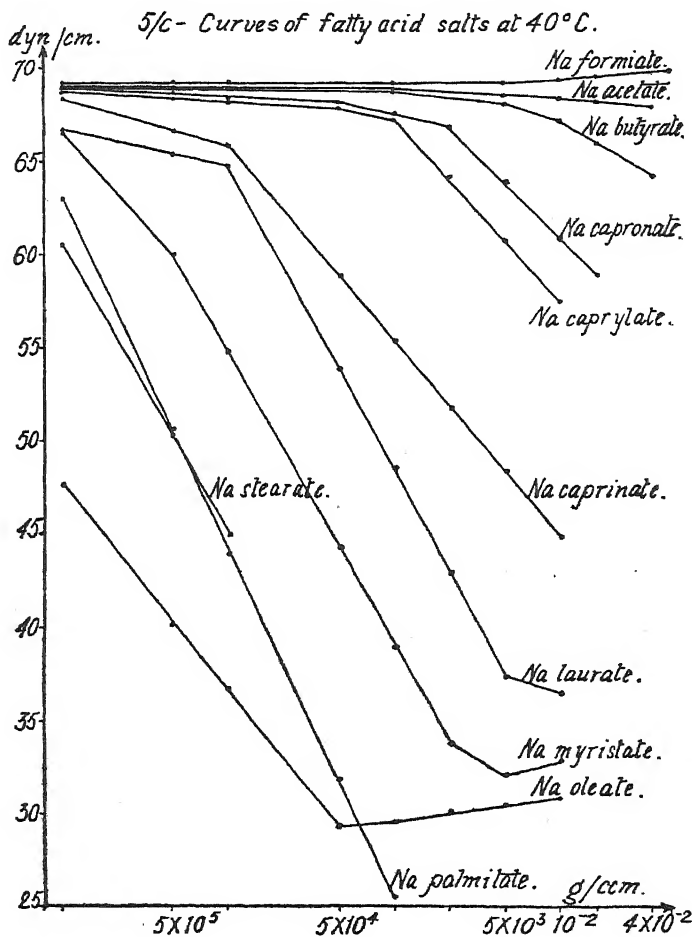


FIG. 3.

is smaller than that of salts of the saturated fatty acid. Within a certain limit of concentration the $\sigma/\log c$ relationship is again linear, but the capillary activity of the oleate is stronger than that of salts of the saturated fatty acid.

**Speed of Equilibration of the Static Surface Tension.**—After having ascertained, that atmospheric $CO_2$ can so seriously affect the surface tension measurements, we became doubtful of the correctness of the measurements of several authors as to the speed of equilibration

of the surface tension of soap solutions. We have, therefore, repeated them under exclusion of $CO_2$.

A soap solution, the surface tension of which had previously been measured, was vigorously stirred and at a short, measured time after giving up the stirring, tested again for its surface tension. These measurements were repeated, until the initial tension was reached again.

We found that the static surface tension of all the soaps tested attains final equilibrium within one minute. Thus, it is not necessary to wait for periods up to half an hour as former authors have reported; the authors did not have regard to the influence of carbonic acid. Our measurements have been semi-quantitative only because it was not possible, for want of apparatus, to keep the time interval constant between the cessation of stirring and the first measurement. However, we have been able to ascertain that it was impossible to measure the time of equilibration of sodium formate up to the laurate, as this was probably too small. Later on in the series the equilibration time became the longer, the higher the number of C-atoms of the fatty acid, the more dilute the solution and the lower the temperature. Consequently all factors diminishing the speed of diffusion increase also the time of equilibration of the surface tension. It was interesting to observe, that the oleates have a slower speed of equilibration than the corresponding salts of saturated fatty acids. Perhaps this is connected with the complicated lay-out (folded together like a pocket knife) [2] of the oleic acid molecules at the boundary surface between water and air.

## GENERAL DISCUSSION.

**Dr. N. K. Adam** (*London*) said : Professor Lottermoser's remarks on the influence of carbon dioxide on the surface tension of soap solutions are very interesting and would appear explicable in the way he suggests, *i.e.*, a chemical interaction between the carbon dioxide and the soap liberating some free fatty acid.

Mr. H. L. Shute and I have recently encountered a mysterious slow change of surface tension with time, in very dilute solutions of long chain colloidal electrolytes, such as the alkyl pyridinium and alkyl trimethyl ammonium bromides, with alkyl groups 12 or 16 carbons long, and potassium cetyl sulphonate. In the absence of added salt, in solutions of 0·025 per cent. or less, the surface tension falls extremely slowly, reaching its final value, of the order 30-36 dynes per cm., only after several days. At 50°, for instance, a 0·01 per cent. solution of cetyl pyridinium bromide showed a surface tension of 55 dynes per cm. five minutes after the surface was formed, 49·7 dynes at three hours, 48 dynes at nine hours, 40 dynes at sixty hours, and reached a final, nearly steady value of about 36 dynes after 150 hours. Stronger solutions show a more rapid attainment of *approximately the same* final surface tension ; with 0·1 per cent. solutions the change (if any) is complete in a few minutes at most; weaker solutions reach equilibrium still more slowly.

Measurements have been made by the method of " sessile bubbles " ; this method appears to be the only one which is almost unaffected by contact angle and can be used for observing very slow changes in surface tension : occasional checks by the method of maximum bubble pressure, which we have modified so as to give readings on surfaces

[2] H. Langmuir, *cf.* L. Lederer, *Kolloidchemie der Seifen*, Dresden, 1932, p. 213.

from five seconds to ten minutes old, have confirmed the results in the very early stage of the fall ; Mr. R. C. Brown has also shown the existence of the slow fall by the ripple method. The precise speed of fall has not yet been found to be reproducible except as regards the order of magnitude of the surface tension at a given time : this is not surprising as accidental convection currents, vibrations, and slight changes of area of surface due to changes in volume of the bubble, were not controlled.

The slow fall is due to an " ageing " of the *surface*, not of the whole solution ; a new bubble blown in a solution, in which the fall of surface tension at the surface of a bubble has been followed for several days, begins at a high value of surface tension and falls to a low value, following approximately the course of the first bubble.

We have further found that almost any salt enormously accelerates the rate of fall of surface tension, the final value being usually attained in a few minutes at most, with $N/20$ solutions of added salt. Carbon dioxide tends to accelerate the fall.

At present the slowness of attainment of equilibrium appears very difficult to explain, as also is its enormous acceleration by adding salt. The amount of salt added is almost certainly insufficient to decrease the solubility of the colloidal electrolyte to such a point that salting out would commence, although it may conceivably affect the degree of aggregation. Any suggestions as to the cause of this effect must necessarily be speculative ; we intend to try and test, in the near future, whether it can be traced to changes in orientation of the molecules in the surface film, by using much longer chain homologues in the form of insoluble unimolecular films ; whether it can be correlated with the degree of aggregation of the colloidal ions in the solution ; and whether it is affected by electrical forces in the neighbourhood of the surface.

**Mr. R. C. Brown** (*London*) said: As Dr. Adam has remarked I have been making measurements of the surface tension of cetyl pyridinium bromide by the method of ripples. It had occurred to us that it would be interesting to compare his results, obtained by the sessile bubble method, with those given by such an entirely different method as that of capillary waves.

In the case of aqueous solutions of low concentration (0·003 per cent.) the surface tension fell with time in much the same way as reported by Dr. Adam and Mr. Shute, but rather more rapidly. When the cetyl pyridinium bromide was dissolved in $N/20$ sodium bromide, it was apparent that the surface tension was falling rapidly during the first few seconds of the life of the surface, but no measurements could be taken until it was about one minute old, by which time it had reached the equilibrium value of about 30 dynes per cm.

I was particularly anxious to try these two solutions, as one of my objects in working on the ripple method was to investigate the effect of the passage of the ripples upon the nature of the surface. The only reference to this problem which I can find is a footnote in Professor Freundlich's book *Colloid and Capillary Chemistry* (English translation of third German edition, page 51). It reads: " One might suppose that the method of surface waves leads to dynamic values. This is not the case as soon as the waves have formed properly. These new molecules of the liquid do not come continually into the waves ; those remain, for the most part, which were originally present." No reference to experimental evidence, however, accompanies this statement.

If a surface, when left to itself, requires a finite time to reach a state of equilibrium, then the passage of a train of waves across it might prevent this process even from beginning, in which case its tension would remain that of the pure solvent.   On the other hand, it might prevent its completion, in which case the surface tension would be intermediate between the final static and initial values, and would presumably depend on the frequency of the waves.   Finally, there is the possibility that the attainment of equilibrium is in no way affected by the waves.   The results seem to indicate that the third possibility is what actually happens, inasmuch as the solutions reached the same constant surface tension as is given by the sessile bubble method, and the values, as far as could be judged, were independent of frequency, although a range of 50 to 300 cycles per sec. was used.

It seems, therefore, that the ripple method is not a dynamic method in the sense in which that of vibrating jets was found to be by Rayleigh. He found that this method gave values of the surface tension of sodium oleate solutions equal to that of pure water.   It is hoped to investigate this point further.

It is worth remarking that the fall of surface tension with time was accompanied by an increase in the damping of the waves, a completely aged surface being much more resistant to their production than a pure water surface.

**Mr. R. C. Murray** (*London*) said : The minima in the surface tension-concentration curves of soaps presented by Professor Lottermoser appear to be characteristic of long-chain colloidal electrolytes, having been found not only in all ordinary soaps [1] but also in alkyl sulphates [2] and alkyl benzene sulphonates.[3]

The existence of a minimum of surface tension in the ordinary soaps might well be thought to be due to hydrolysis, as indeed was suggested by Ekwall.[4]   This seems to be largely disproved by Professor Lottermoser's present results, and in any case cannot explain the presence of similar points in the curves for unhydrolysed substances such as the alkyl benzene sulphonates and alkyl sulphates.

The law of mass action when applied to the equilibria in solutions of colloid electrolytes, offers a simple explanation of this peculiarity. Suppose we are dealing with a long-chain salt, which will be represented here as a sodium salt NaX, and that the unassociated fraction of NaX suffers complete ionic dissociation ;   then we shall have present in the solution three solute species :  (1) Ionic micelle ;  (2) simple Na ions ; (3) simple X ions.   Since the high charge of the micelle will undoubtedly cause inclusion of a few Na ions in them, the second and third species will not be present in equivalent proportions.   Under these circumstances, by means of the methods outlined by Murray and Hartley [5] we find that, as shown in Fig. 1, the concentration of micelles rises very rapidly, and that of simple Na ions moderately slowly, as the total concentration increases, but that the concentration of simple long-chain ions reaches a maximum, at just beyond the point where the rapid increase of micellar concentration sets in.

Now Lottermoser and Puschel found that the minimum of surface

[1] See also Lottermoser and Tesch, *Koll. Beiheft.*, **34**, 339, 1931 ;  E. G. Walker *J.C.S.*, 1521, 1921, *et al.*
[2] Lottermoser and Püschel, *Koll. Z.*, **63**, 174, 1933.
[3] Neville and Jeanson, *J. Physic. Chem.*, **37**, 1001, 1933.
[4] Ekwall, *Acta. Acad. Aboensis.*, iv., N : 0·1, 1927.          [5] *This vol.*, p. 183.

tension of the alkyl sulphates occurred at a little beyond that concentration at which a very sudden change of direction of their conductivity curves occurred, which is attributable to the rapid increase in micellar concentration.

The suggestion therefore is that the surface activity of colloid electrolyte solutions is determined almost entirely by simple long-chain ions, the micelles playing little or no part in the depression of surface tension. This difference in behaviour of the two units may be due merely to the fact that the micelles, though present in the surface, are, on account of their size, not very numerous ; or it may be that they are more soluble than the simple long-chain ions, which is a much more likely hypothesis. The simple ions are charged, and therefore hydrophilic, at only one small point on their periphery, the remainder of which has very little affinity for water ; these will no doubt be present in the surface with only their charged part below it. The micelle, however, must be thought of as having an exterior completely hydrophilic on account of the approximately equal distribution of charge on it. This would render the aggregate more soluble. In fact, it resembles in some ways an ordinary inorganic ion, which, as is well known, shows negative surface sorption in water.
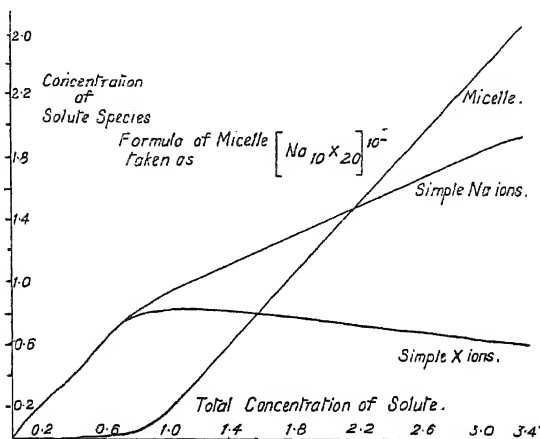


FIG. 1.

I do not think that the behaviour of a foam can, at any rate in our present state of knowledge, be adduced as evidence for the nature of the surface active units in solutions of these long-chain salts. This stability is dependent on at least two other factors besides the surface activity, namely the vapour pressure and viscosity. The large decrease in the latter, and increase in the former, consequent on a rise of temperature, both act in a direction tending to decrease the stability of the foam, in a measure which would probably quite outbalance the effect of a change in surface activity, whatever the direction of this change should be.

In connection with this, it is of interest to note that Dr. Lawrence [5] has obtained experimental evidence that the soap in soap films is present in the monomeric form.

**Dr. W. Ramsden** (*Oxford*) said : It would be of interest to know whether the surface-regions studied by Dr. Adam and Mr. Shute resemble those of aqueous solutions of saponin in being " rigidified " by the adsorbate, and if so whether they become " rigid " before they have attained equilibrium.

(*Added later.*) By a " rigidified " surface-region he meant one which did not yield appreciably to a sufficiently small surface-parallel stress

[5] A. S. C. Lawrence, *J. Physic. Chem.*, 263, 1930.

during ten or more minutes, one which must therefore be either " solid " or " almost solid " along surface-parallel axes. With surface-regions whose adsorbates formed " rigidifying " structures before adsorption was complete the accession of the additional molecules required for equilibrium was likely to be very slow.

**Dr. N. K. Adam,** in reply, said : I am afraid I have no data yet as to whether or not the adsorbed films become rigid, but Professor Ramsden's suggestion ought certainly to be tested.

**Professor A. Lottermoser** (*Dresden*) (*communicated*) in reply, said : The remarks of Dr. Adam and Mr. Brown on the change of surface tension with time in solutions of pyridinium and alkyl trimethyl ammonium bromide are extremely interesting. The change must be real, because these authors have found the same change by different methods. I have not found hitherto any change of surface tension of sodium soap solutions with time with the pull-off ring method, but I have observed that the surface tension of potassium soap solutions do not become constant with time : a very mysterious and inexplicable fact.

Mr. Murray has said that the simple fatty acid ions diminish the surface tension of water and not the aggregates. The former fact is in agreement with my measurements. I had thought, however, that, on the contrary, the aggregate ions effect a change of surface tension. The fact that the soap foam is very stable, but becomes more and more unstable with increasing temperature and finally disappears would accord with this view. Professor McBain has shown that the aggregation in soap solutions is diminished with increasing temperature.

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# SOME INDUSTRIAL APPLICATIONS OF COLLOIDAL ELECTROLYTES.

By A. Stewart and H. M. Bunbury.

The last decade has witnessed the development and application of a range of synthetic organic products, which in solution exhibit remarkable surface active properties in various directions. These materials, although developed primarily for use as assistants in the processing of textiles have, on account of their unusual properties, found applications in many other branches of industry. It is the aim of this paper to survey briefly the nature of these new products which, until recently were little more than chemical curiosities, and to indicate their main properties and applications.

The sulphonated oils, for example the familiar Turkey Red Oil, which is a sulphonated castor oil, were probably the earliest textile assistants to come into prominence, being used to replace rancid olive oil in the dyeing of Turkey Red. Methods were later on devised for the sulphonation of cod oil to give products which are miscible with mineral oils under certain conditions, the miscible product forming an emulsion when mixed with water, and are of particular value for treating leather after tanning.

When castor oil is sulphonated for the production of Turkey Red Oil, many reactions take place, including the addition of sulphuric acid at the double bond to give a sulphuric acid ester, and some sulphation of the hydroxyl group of the ricinoleic acid, hydrolysis of this ester group to give hydroxyl groups, partial hydrolysis of the triglyceride to give

mono- and di-glycerides and free carboxylic acids, polymerised products, lactones, etc.  The chemistry of the sulphonated oils has not, however, even yet been entirely elucidated.

Turkey Red Oils are still widely used as textile assistants on account of their " solubilising " action on many organic materials, their property of increasing the penetration of dye liquors, and their use as softening agents for textiles.  Turkey Red Oil, however, is only slightly more stable to dilute acids and hard waters than is soap, and one of the recent developments in this field has been changes in the method of sulphonation and modification of the carboxylic acid group to give more highly sulphonated products containing in some cases the true sulphonic acid group $C—SO_3Na$.  These products are remarkably stable to solutions of mineral acids, alkalies, metal salts, and hard water.  In general, this change in the sulphonated oil products has had the effect of reducing the emulsifying action, but considerably increasing their wetting action.  These compounds find applications under conditions in which the Turkey Red Oils are unstable.

In 1911 Stiasny showed that certain condensation products of aldehydes with aromatic and phenolic sulphonic acids had the property of tanning leather, that is, rendering the hide proteins insoluble, and a large range of products were investigated for this purpose.  Subsequently, it was found that similar preparations, of which dinaphthyl-methane-disulphonic acid is a typical example, had a pronounced so-called dispersing action.

The introduction of lower alkyl groups into aromatic sulphonic acids was shown in 1917 to give products, e.g., isopropylnaphthalene sulphonate, which in solution had a remarkable surface activity and exhibited certain soap-like properties.  This led to the preparation of a great variety of products containing different alkyl groups and aromatic nuclei, and a large number of such products are now marketed for various purposes.  These are mainly the ethyl, isopropyl, and butyl homologues of sulphonated naphthalene, naphthene, abietene, octahydroanthracene, and similar substances, and they owe their importance mainly to their pronounced wetting out action combined with their high stability and solubility in acids and metallic salt solutions.

Since 1930 the most important development in this field has been the introduction of compounds which, like soaps, have a long alkyl chain, but in which the carboxylic acid group has been replaced.  Many are derived directly or indirectly from the higher aliphatic alcohols containing from 12 to 18 carbon atoms, the best known of these alcohol derivatives being the salts of the sulphuric acid esters, $R—O—SO_3—M$, where R is the alkyl chain and M is sodium, potassium, ammonium, or an amine, e.g., triethanolamine.  Others are of the type $R—CO—X$, derived from a higher fatty acid, X being a further radicle containing almost invariably a sulphonic acid group, e.g., $R—CO—NH—CH_2CH_2SO_3Na$.  Other compounds in this general class contain other " bridging " groups, such as —NH—, —S—, etc.  A further class of compounds which show many unique properties are the long chain quaternary ammonium compounds $R—N(R_1)_3Y$ where R contains a long alkyl chain, $R_1$ a short chain or radicle, and Y a salt-forming group.  It will be noticed that in this latter class the long chain is contained in the cation, e.g., $C_{18}H_{37}—N(CH_3)_3 +$ ... $Cl^-$ or $C_{18}H_{35}CONH.CH_2CH_2—NH(C_2H_5)_2^+$ ... $Cl^-$, whereas in the other types mentioned above the long chain is contained in the anion, e.g., $R—O—SO_3^-$ ... $Na^+$ or $R—CO—O—CH_2CH_2SO_3^-$ ... $Na^+$.

The colloidal behaviour of these new surface active agents has received little attention, although their treatment in the technical or patent literature has been voluminous, over 200 English Patents relating to such materials appearing in a single year. Sufficient work has, however, been carried out to show that certain of these new agents are colloidal electrolytes, while the colloidal properties of others is still a matter for further investigation.

Norris[1] from a study of the electrical conductivity and osmotic activity of solutions of cetyl sulphonic acid, determined that this material had the typical behaviour of a colloidal electrolyte, similar to that of the higher soaps, and far surpassing the colloidal properties of aromatic sulphonates containing a similar number of carbon atoms. Lottermoser and Pusdel[2] examined the electrical conductivities of solutions of the free acids and metal salts of long chain alcohol sulphuric esters containing from 12 to 18 carbon atoms, finding that the conductivity concentration curves showed maximum and minimum values the position of which depended on the chain length. The surface tension and interfacial tension of these alcohol sulphuric ester salts have been examined by Lottermoser and Stoll.[3]

Neville and Jeanson[4] investigated the surface tension of solutions of various alkylated benzene sulphonates, determining the pronounced effect of the side chain on surface activity. The same workers also examined the adsorption of scouring agents of the type of $R$—$O$—$SO_3Na$ and $R$—$CO$—$NH$—$CH_2CH_2SO_3Na$ on wool at different $p_H$, and the effect of such adsorption on the taking up of acid and basic dyes by the wool.

Schramek and Velten[5] investigated the action of certain wetting agents in their application to dyeing and printing anthraquinone vat colours, and determined the relative efficiencies of the various agents in protecting dyestuff sols from precipitation by electrolytes. Bertsch[6] has attempted to relate the activity of surface active materials to the colloidal character of the polar groups in the agent.

Smith and Jones[7] showed that considerable errors occur when the $p_H$ is measured by colorimetric methods in the presence of various scouring and wetting agents. Mosher,[8] Burton and Robertshaw,[9] and Hartley[10] showed similar errors in the cases of soap solutions, sulphonated oils, and the long chain quaternary ammonium salts.

## Industrial Applications.

The principal industrial applications of these new agents are in connection with detergent treatment, wetting out, emulsification of oils, and the preparation of aqueous suspensions.

(a) **Alkylated Aromatic Sulphonates.**—The main application of these agents is for wetting out and, in general, changes in the alkyl group alter the intensity of the wetting action. Condensation products

[1] Norris, *J. Chem. Soc.*, **121**, 2161, 1922.
[2] Lottermoser and Pusdel, *Kolloid Z.*, **63**, 175, 1933.
[3] Lottermoser and Stoll, *Kolloid Z.*, **63**, 49, 1933.
[4] Neville and Jeanson, *J. Physical Chem.*, **37**, 1001, 1933.
[5] Schramek and Velten, *Kolloid Beihefte*, **34**, 80-114, 1932.
[6] Bertsch, *Melliands Textilberichte*, **11**, 779, 1930.
[7] Smith and Jones, *J. Physical Chem.*, **38**, 243, 1934.
[8] Mosher, *American Dyestuffs Reporter*, **19**, 261, 1930.
[9] Burton and Robertshaw, *J. International Soc. Leather Trades Chemists*, **18**, 19, 1934.
[10] Hartley, *Trans. Faraday Soc.*, **30**, 444, 1934.

of aldehydes with aromatic sulphonic acids have strong dispersing and tanning actions, but have very poor wetting properties.

(b) **Sulphuric Acid Ester Salts of Long Chain Alcohols and Related Compounds.**—Compounds containing a chain length of less than 10 carbon atoms have little surface activity, those containing 12 carbon atoms have good wetting out properties, and with increasing chain length up to 18 carbon atoms the wetting action decreases slightly and the detergent properties are increased. Compounds with the sulphuric acid ester group situated in the middle of the chain have a lower detergent action than when the group is terminal.

(c) **Sulphonated Oils.**—Oils of the type of Turkey Red Oil are good emulsifying and " solubilising " agents, and comparatively poor wetting agents save in strongly alkaline solutions. Their solutions have a low stability to acids, hard water, and metal salts. The more highly sulphonated oils, and modified oils, are generally less effective emulsifying agents, but have a much greater wetting action, particularly under acid conditions. Their solutions are less readily salted out, and have a much greater stability to acids, hard water, metal salts, and alkalies.

(d) **Long Chain Quaternary Ammonium Compounds.**—Compounds having a 12 carbon atom chain have a wetting action, and with increasing length of chain the wetting action decreases, but such compounds show considerable detergent action when used under acid conditions. In general, however, the properties of this type of compound are more specific to the particular constitution than are other types of compound.

## Application as Detergents.

The application of certain of these new products to the cleansing of all kinds of textiles and other materials, is probably the most remarkable of recent developments. Agents widely used for this purpose are the sulphuric acid ester salts of long chain alcohols and the condensation products of higher fatty acids with short radicals containing sulphonic or sulphato groups.

These materials have come rapidly into prominence because in addition to possessing extraordinarily high detergent power they have certain properties which enable the processing of the textile material to be more simply carried out. (a) The new agents are stable in hard waters. With agents which are unstable under hard water conditions it is difficult to avoid a precipitate forming on the goods, giving a poor appearance, and causing uneven results to be obtained in any subsequent dyeing operation. The new agents avoid this defect, and actually many of them have the property of dispersing a deposit, e.g., of alkaline earth soaps already present on the goods. (b) The agents improve the appearance and " handle " of textile material, leaving them in a soft and open condition, and in the case of woollen goods minimising felting. They do not turn rancid. (c) The stability of the new agents to dilute acids enables them to be employed in acid dyebaths. Their presence in the dyebath promotes level dyeing, increases penetration, and improves the general appearance, and an added advantage is that small amounts of the detergent remaining in the textile from a previous scouring operation have no deleterious effect in an acid dyebath, whereas any soap remaining in the goods would require to be completely removed. (d) The new agents give neutral solutions, and can be used with delicate materials such as artificial silk goods without any danger of damage.

The detergent agents generally show their maximum action under alkaline conditions, although they may also be used under neutral or slightly acid conditions. As mentioned above, the long chain quaternary ammonium compounds are exceptions to this rule, having their maximum action under acid conditions.

## Wetting Agents.

These are materials which, even when present in very small amounts, e.g., 0·05-0·5 per cent., give aqueous solutions, the property of wetting materials which are strongly resistant to being wetted by water. Examples of such surfaces are raw cotton or wool, painted or waxy surfaces, and certain insoluble powders, such as sulphur and indigo. Since complete wetting out is required whenever such materials have to undergo some uniform aqueous treatment, the value of these new assistants in reducing the time of an otherwise lengthy wetting operation requires no elaboration.

The large range of these agents available includes practically all types of surface active compounds described above. Those most widely used are the alkylated aromatic sulphonates ; sulphonated oils, particularly those belonging to the highly sulphonated class ; and mixtures of these materials with organic solvents such as cyclohexanol, tetrahydronaphthalene, or pine oil, to increase the wetting action.

An interesting feature of the wetting phenomenon is the changes in wetting activity shown by various agents in solutions of different $p_H$. In wetting properties Turkey Red Oil is comparatively poor under neutral or acid conditions, but is much better under alkaline conditions. Certain of the highly sulphonated oils show their maximum effect under acid conditions, others in neutral or in alkaline conditions, depending on their particular composition. The alkylated aromatic sulphonates have their maximum action under acid conditions, but retain a high activity up to moderately strong alkaline conditions.

Wetting agents are applied under acid conditions when used in the acid dyebath to assist in penetration, and to obtain more level results. The mercerisation of cotton is an example of the application of wetting agents under strongly alkaline conditions. In this process the cotton is passed through a solution of 20 per cent. to 27 per cent. caustic soda. The addition of a wetting agent considerably accelerates the speed of wetting and penetration, and gives more uniform results. The increased wetting activity also enables goods to be mercerised without preliminary boiling out, which would otherwise be too resistant to wetting to be so treated. Certain highly sulphonated oils are suitable for use in mercerising, but the type of agent more general employed consists of a mixture of phenolic bodies with organic solvents such as cyclohexanol, or monoethylglycol ether.

Applications of wetting agents under substantially neutral conditions are very numerous. In the textile industry they are used to wet out raw cotton, wool, and other raw materials ; to increase the uniform penetration of treating liquors, particularly into closely woven material ; as addition to vat dyestuff baths to prevent the formation of a scum of oxidised dyestuff at the surface of the bath ; and for wetting out powders used in preparing the dyebath.

The alkylated aromatic sulphonates are of particular interest in laundry work. Normally, before the goods receive any washing treat-

ment they are subjected to what is termed a " breakdown " for the purpose of removing old starch, etc. This is carried out by soaking the goods in water, and may include treatment with a malt preparation to assist in the removal of the starch. This preliminary breakdown may often be omitted without detriment if the wetting agent is added to the first washing bath, on account of the rapid wetting out produced, and the beneficial action of the agent in assisting the removal of old starch and dirt from the goods. An actual large scale trial showed that the use of a wetting agent reduced the time occupied in washing collars by 30 per cent.

Other more general applications of wetting agents are as spreading agents for horticultural sprays ; to assist in the washing of painted or waxy surfaces ; to render powders readily wettable with water ; and for overcoming the difficulty of wetting furs before treatment, a process which must be carried out at low temperatures, and which without the use of wetting assistants is very protracted.

### Dispersing Agents.

Many materials which are insoluble in water are used as finely divided aqueous suspensions, the majority of particles being generally between $0\cdot3\text{-}3\mu$ in size, with occasional larger particles up to $30\text{-}50\mu$, and such materials are frequently marketed in the form of pastes. Examples of such products are vat and acetate silk dyestuffs, pigments, compounding ingredients for use in rubber latex processes, and horticultural insecticidal preparations. In the preparation of these suspensions a group of compounds termed " dispersing agents " plays an important part, such agents belonging to the type of sulphated long chain alcohols and related compounds, sulphonated oils, condensation products of aromatic sulphonates with aldehydes, e.g., dinaphthylmethane-disulphonate (obtained by condensing sulphonated naphthalene with formaldehyde), sulphite cellulose lye and modified forms of this material. Soaps and proteins are also used, but in general they have certain disadvantages in comparison with the synthetic products.

The required state of subdivision of the suspensions is obtained by mechanical disintegration, or by control of the particle size during formation. Dispersing agents are sometimes added during the formation of the particles when they exert a protective colloid action giving a finer state of subdivision ; the more general application of the agents is, however, in conditioning the physical properties of the suspension.

The particles in a finely divided suspension of an insoluble organic material in water aggregate strongly together, giving the paste a coarse appearance, and addition of a small amount of dispersing agent reduces this strong aggregation and improves the paste appearance. A further application is for reducing the viscosity of very thick pastes.

Commercial paste suspensions generally contain from 10 per cent. to 50 per cent. of the disperse phase. Unlike lyophobic sols, these are stable when flocculated, and generally unstable when deflocculated, the reason being that the suspensions contain particles of such a size that under conditions of deflocculation they settle out, whereas when slightly flocculated the net-work structure of particles formed can generally be controlled so as to hold up the larger particles. Even when these particles are too large to be suspended in this manner, on settling they form only a loose deposit at the bottom, whereas the same particles settling out from a deflocculated suspension invariably form a heavy " clay-like " deposit.

From a dilute suspension the deflocculated particles settle out, leaving a clear aqueous layer. The concentration of the sediment is however fairly low, depending amongst other factors on the particle size, shape, and extent of flocculation ; decreasing flocculation, as is obtained by the addition of dispersing agents, increases the concentration of the deposit. It is therefore possible to adjust the suspension so that the natural concentration of the sediment is equal to or less than the concentration at which it is desired to market the paste, under which conditions a stable product is obtained. The " viscosity " of the product increases as its concentration increases above that of the settling concentration from dilute suspension in a similar medium. The " viscosity " is also affected by the uniformity of the flocculation, a suspension containing particles which are tightly clustered together always having a lower value.

Dispersing agents probably owe their effect to being strongly adsorbed at the particle surface with their hydrophylic polar groups orientated towards the water phase. The hydrophobic nature of the surface is thereby decreased, with a corresponding decrease in those attractive forces which are the cause of flocculation. The agents probably also increase the charge on the particle, normally negative, and when present in sufficient amount cause deflocculation. As would be anticipated, the addition of electrolytes causes flocculation of the deflocculated particles. The amounts required to counteract the addition of dispersing agents are, however, remarkably large. A dyestuff suspension in a $1/1000$ molar solution of dinaphthylmethane disulphonate required a $1/125$ $N$ concentration of sodium chloride just to produce flocculation, and in a $1/500$ $M$ solution of the agent the concentration of salt is $1/50$ $N$. By employing a mixture of electrolyte and dispersing agent it is possible to obtain a concentrated paste in the flocculated condition, but which becomes deflocculated on dilution.

When paste suspensions are evaporated to dryness, they cannot be reformed into a suspension without intensive mechanical treatment. Certain dispersing agents when incorporated into the suspension before evaporation enable a dry product to be obtained which is readily wetted with water, and substantially reforms the state of subdivision of the original suspension.

Although as mentioned above the majority of these suspensions carry a negative charge, it is possible by employing the long chain quaternary ammonium type of compound to prepare suspensions having a positive charge.

## Emulsifying Agents.

Many of the surface active agents described above are excellent emulsifying agents, and certain of their applications in this connection deserve special mention.

The majority of the sulphonated oil preparations have the property of being miscible with many organic liquids to give clear fluid products containing up to about 80 per cent. of the added liquid, and when suitably prepared the products readily form emulsions, or in some cases give clear solutions, even though the added liquid was immiscible with water. Such preparations are widely used as wetting agents, as assistants in the dyebath, and in the leather industry.

Certain of the agents which themselves are somewhat poor emulsifying agents act as powerful emulsifying assistants when used in conjunction

with other substances. The alkylated aromatic sulphonates are an example of this assistant action, mixtures with soaps or with protein materials having an exceptionally good emulsifying action.

Agents such as the sulphated long chain alcohols, or Turkey Red Oils, in addition to having an emulsifying action, impart a soft handle to treated goods. They are used to emulsify certain oily and waxy material to give products which are extremely valuable as softening agents in finishing.

They are also effective in stabilising rubber latex, particularly under acid conditions, or when compounded.

**Other Applications.**—A number of specialised applications falling outside the foregoing general groups are worthy of mention.

Condensation products of aldehydes with aromatic and phenolic sulphonic acids having a tanning action when added to a protein solution, *e.g.*, gelatine give a solution which when acidified forms a precipitate which readily redissolves on addition of alkali. This behaviour is sometimes made use of when it is desired to filter off a finely divided suspension or colloidal solution, and subsequently to reproduce the initial state of dispersion ; a small amount of protein and synthetic tanning agent is added to the suspension and then acidified, when the precipitate formed carries down with it the suspension in a filterable form. After filtration, the original state of dispersion is substantially reproduced by mixing the filter press cake with a solution of alkali.

The general class of aromatic sulphonates have the property of peptising solutions of proteins, *e.g.*, casein or glue, and the alkylated naphthalene sulphonates are particularly effective for this purpose.

Certain of the long chain alkyl amine compounds show a number of curious properties, some of which find technical application. These include their use as : (1) Inhibitors for preventing iron being dissolved by mineral acids, a behaviour which is applied in the pickling of iron by acid to remove rust and scale, *e.g.*, before tinning, with the minimum loss of metallic iron. (2) Agents to assist in the removal of colours from incorrectly dyed or printed material, from rags before reworking, or from unwanted stock. For a large number of dyestuffs the colour can be effectively removed by a so-called " stripping " treatment, in which the goods are treated in a solution of a strong reducing agent (*e.g.*, alkaline sodium hydrosulphite), or oxidising agent. The addition of these agents has a most remarkable promoting action in the stripping process, enabling a considerable number of dyes to be completely removed which would otherwise resist the stripping treatment (*e.g.*, Azoics, *i.e.*, insoluble azo pigments produced on the fibre by coupling an alkaline salt of a $\beta$-hydroxy naphthoic arylide with a diazotised base. These dyestuffs are characterised by possessing a very high washing fastness and resistance to removal from the fibre. (3) Other agents of this type have the property of increasing the fastness of direct dyestuffs on cotton or viscose towards water, acids, or perspiration. This action confers many advantages in the processing of such dyed or printed material.

## Summary.

The applications of some of the newer types of synthetic organic compounds possessing pronounced surface-active properties are briefly reviewed and their growing industrial importance indicated.

## GENERAL DISCUSSION.

**Professor E. Elöd** (*Karlsruhe*) said : In considering the influence of wetting agents on the taking up of dyestuffs, we must strictly distinguish between the dyeing of woven material on the one hand and of single fibres on the other. The dyeing of woven fibres (and especially its " even dyeing ") depends to a great extent on the wetting qualities of the surface of the woven material and also on those of the fibres lying in the interior of the tissue. This latter wetting quality is improved by the wetting materials. In contrast to this, the penetration of the dyestuffs into the single fibres and also the velocity of its diffusion is only slightly or rarely influenced by the presence of the wetting agents. The penetration of the dyestuffs (*e.g.* in cellulose fibres) is chiefly dependent on the degree of dispersion of the dyestuff and on the free spaces, *i.e.* on the pores of the fibres. Dispersion is only in exceptional cases changed by wetting agents ; the sizes of the pores are never changed.

# PART II.   (B) DYESTUFFS.

# INVESTIGATION OF CHEMICAL REACTIONS IN GELATIN BY MEANS OF MEASUREMENTS OF LIGHT ABSORPTION.

## (XXI. COMMUNICATION CONCERNING MORDANTING AND DYEING PROCESSES.)*

By E. Elöd and Th. Schachowskoy.

(*Technische Hochschule, Karlsruhe.*)

From a purely phenomenological point of view, the action of Cr-III-, Fe-III-, Al-III-, etc., salts on proteins, such as collagen and gelatin (*i.e.,* " tanning " or " hardening ") probably belongs to the most generally known processes, but the setting up of a satisfactory theory for the resulting phenomena still meets with considerable difficulties. The reasons for this are in part due to the fact that in tanning the transformation of the protein substance (*i.e.,* of collagen) into the tanned product (*viz.,* leather) goes through many partial processes. The study of these partial processes is rendered especially difficult by the macroscopic structural nature of the collagen substance. The metal salts required for tanning are found in the solutions employed, in a labile condition (hydrolysis), and gradually undergo changes while they are being diffused into the interior of the skin substance. Accordingly, apart from a few special cases, the process of tanning may be expected to take place in layers, both as concerns the cross-section of the skin and the cross-section of each single collagen fibre itself.

The requirement that each single fibre, even each micelle, should be brought into interaction with mineral tanning substances cannot experimentally be fulfilled with ease. The result of this is, that in finding out

* XX. Comm., see *Collegium*, 414, 1934.

the causes of the phenomena manifested in tanning, it is expedient first to start with suitable model experiments rather than to examine the tanning of the collagen material itself.   Only in this way can a decision be come to as to the composition of the metal compounds which have a real tanning effect and on *the nature* of the interaction of these compounds with protein substance.   The analytical comprehension of the condition of metal compounds in leather may easily lead to a false conclusion, and offers extensive possibilities for the subjective conception of the experimentalist.

The model experiments we have carried out in seeking an explanation of these processes were directed, in the first place, to the distribution of the metal compounds in the cross-section of the protein fibres.   In the investigation of the action of aqueous solutions of $SnCl_4$ on *natural silk* (" loading " process), these led to the result that even in the case of those very thin, isolated single fibrils, the above-mentioned difficulties (as to the equal distribution of metal compounds in the cross-section of single fibres) were plainly evident, and that according to the selected conditions, these affected the result to a greater or less degree.   The distribution of the tin hydroxides in silk can be diagrammatically represented by
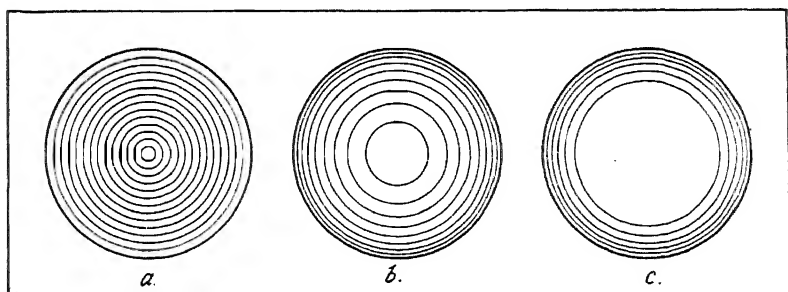


Fig. 1.—Schematic picture of the distribution of deposits in the cross-section of the fibre: (*a*) uniformly; (*b*) predominantly in the outer layers; (*c*) only in the outer layers.

microscopic investigation of microtome sections of ash skeletons,[1] as shown in Fig. 1.   In the primary process it is really present in the fibre as free $Sn(OH)_4$, as can be deduced from X-ray diagrams, which showed, in addition to the unchanged fibre diagram, the diagram of $SnO_2$.[1a]   The further study of this problem of these investigations made it desirable to carry out other model experiments on protein material, which shows no macroscopic structure.   For this purpose, gelatin (genetically related to collagen) was chosen.

It was evident from the first that for the investigation of the interaction between protein and metal compounds (that is, of the actual condition of the metal compounds during their tanning action) such methods must be chosen as would serve to provide an explanation of the processes and of the possible conditions without affecting those processes or conditions.

In connection with this, however, it should be taken into consideration, that the selected method must be capable of registering the changes of the metal combinations *during their action on the protein*.   These changes

[1] E. Elöd, E. Silva and H. Schroers, *Mell.*, 782, 1930; and 757, 1932.
[1a] Comp. E. Elöd and E. Pieper, *Z. angew. Chem.*, 41, 14, 1928.

have different causes.  In protein fibres possessing a definite structure, we have to consider the changes in concentration during the diffusion into the interior of the skin (membrane phenomena), the membrane hydrolysis, the capacity of the protein substance for acid combination and other probable adsorptive effects as well as the properties of the metal compounds.  For gelatin the conditions are more evident and the alteration in the metal compounds must be found chiefly in their own character and in their specific protein effect.

From the above-mentioned possible methods of investigation, we have selected the study of the *change of light absorption* of the aqueous as well as of the gelatin containing solutions of the metal compounds.[2]

As is well known, metal compounds, generally of a complex nature, are employed in tanning.  From the literature we know that interesting conclusions can be drawn as to the condition of the complex compounds from the light absorption or from the Raman spectra of these compounds :  these methods causing no structural changes in the conditions of the molecules.[3]

It was interesting to find out whether measurement of the light absorption in Cr-III-, Al-III-, and Fe-III- compounds respectively, in the complex compounds which are used in tanning, makes it possible to decide whether and how far the metal compound is changed in its aqueous solutions by the presence of gelatin.

The question also arose whether such measurements deduce the composition, or the character of the actual tanning metal compounds which are only formed in the presence of gelatin.

## 2.

The measurements of the light absorption were made with the Pulfrich Stufen-photometer of Zeiss.[4]   We chose the simplified method intentionally, but were convinced that for the essential process of following the absorption curve or of its changes, a sufficient number of explanations exist.  Supplementary investigations with the medium sized quartz Hilger spectrograph showed no *essential* deviations of the absorption curves in its characteristic course.  Thus, we could attain our object with the eight light filters, which give a fairly wide spectral range.

In the following passages we shall show by some examples how very different the absorption curves of the metal compounds concerned prove to be, not only among themselves, but also after action on gelatin, in regard to their shape and the position of their maxima.   It is also possible to decide whether the one or the other metal compound employed remains unchanged, or if it has undergone any change.   In some cases, it was even possible to form conclusions on the *manner* of this change (*cf.* cobalt complexes, below).

On account of the unfavourable situation of its absorption band, we have made no further investigations into aluminium compounds.

Since ample data are to be found in literature with regard to the reactions of Fe-III-compounds in aqueous solutions,[5] we were able to

[2] Comp. E. Elöd and Th. Schachowskoy, *Collegium,* 701, 1933.
[3] *I.e.,* B. Smekal, *Z. Elchem.,* 36, 615, 1930 ;  *Nat. wiss.,* 16, 527, 1928 F. Kohlrausch, *Der Smekal-Raman-Effekt.,* 1921 ; F. Damaschun, *Z. physik. chem.,* 16B, 81, 1932 ;  22B, 97, 1933.
[4] Comp. E. Elöd and Th. Schachowskoy, *Koll. Zeitschr.,* 69, 79, 1934.
[5] Gmelin's *Handb. d. anorg. Chemie,* 8. Aufl. System No. 59, 1932.

investigate the relationship between their composition and the tanning action solely from the action of these compounds with gelatin.

Chromium compounds are known to be present in exceptionally diverse forms and characters, of which many are consciously or unconsciously used for tanning, and for these the conditions are less clear. It thus became necessary to characterise the action of such of these compounds as were used by us. We have produced some chromium-III-compounds in a pure form and examined them in the first place qualitatively in their action on gelatin. For this purpose, a 10 per cent. gelatin solution at 35-40° C. was mixed with the solutions of the corresponding chromium complex compounds mentioned in Table I. and then made into films.[6] After undergoing a drying process for twelve hours, test films measuring $3 \times 1.5 \times 0.025$ cm. were pressed on to a smooth aluminium sheet, and treated with a constant and fixed jet of water at a temperature of 42° C. and at the rate of 3·8 litres of water per minute. The time necessary for complete solution in these tests (calculated at 0·1 mm. thickness) shows the time required for the solution of the films examined. In addition to this, the test films were examined by the so-called " boiling test," by immersing them in boiling water for five minutes (compare Table I.).

We will now discuss these purely qualitative results more fully. If we look at the solubility at a temperature of 42° C., we see that $[Cr(CN)_6]K_3, [Cr(C_2O_4)_3]K_3$, $[Cr(NH_3)_6](NO_3)_3$, $[Cr(NH_3)_2(CSN)_4]NH_4$ in contrast to the other complexes scarcely or only slightly affect the solubility of the gelatin, whereas, with the exception of $[Cr(CN)_6]K_3$ they all show a positive boiling test. This, at first glance, apparently strange phenomenon, that a piece of gelatin dissolves readily at a temperature of 42°, but only dissolves with difficulty at 100° C., can be understood, if we compare the colours of the gelatin treated with Cr-III-complexes before and after the boiling test. The strips of gelatin which, according to the colour of the complex employed, were yellow, red, violet or pink, all turned *green* after the boiling test. This purely qualitative result seems to show that, in chromium-III-compounds, it is not the complexes themselves, but their decomposition products which cause the difficult solubility of the gelatin.

TABLE I.—THE ACTION OF SOME CHROMIUM COMPLEXES ON GELATIN.

| Chromium Compound. | Behaviour at | | Colour of the Film. | |
|---|---|---|---|---|
| | 42° C. | Under (5') Boiling Test. | Before Boiling. | After Boiling. |
| $[Cr(CN)_6]K_3$ | Sol. 52 " | — | Colourless. | No change. |
| $K_3[Cr(CSN)_6]$ | Insol. | + | Violet. | Green. |
| $(NH_4)_3[Cr(CSN)_6]$ | ,, | + | ,, | ,, |
| $[Cr(CH_3CO_2)_6]CrO_4CH_3CO_2$ | ,, | + | Green. | ,, |
| $[Cr(NH_3)_5Cl]Cl_2$ | ,, | + | Rose. | ,, |
| $[Cr_3(C_2H_3O_2)_6OH](CH_3CO_2)_2$ | not quite sol. | + | Green. | ,, |
| $K_3[Cr(C_2O_4)_3]$ | Sol. 72 " | + ! | Violet. | ,, |
| $[Cr(NH_3)_6](NO_3)_3$ | Sol. 60 " | + ! | Yellow. | ,, |
| $[Cr(NH_3)_2(CSN)_4]NH_4$ | Sol. 50 " | + ! | Rose. | ,, |

[6] Vide e.g. *Brevet franç.*, Nr. 758,660.

As we know from the literature and from the explanations in a former paper,[7] most complex compounds are more or less thermolabile, according to the kind of bonds. On treatment with water at a temperature of 42°, the chromium-III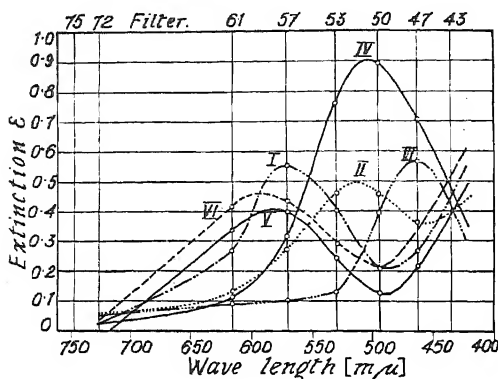-compounds employed are still apparently stable, so that during the time required for solution the quantities of the product produced by disintegration are not sufficient for the tanning of the gelatin. On increasing the temperature to 100° C. (boiling test) the velocity of the disintegrating process is accelerated to such an extent that within a short time (much shorter than that required for the solution of gelatin) sufficient quantities of the actual tanning substance are available for the development of difficult solubility.



FIG 2.—Absorption curves of :—

I. $[Cr(CSN)_6]K_3$.     II. $[Cr(CSN)_4(NH_3)_2]NH_4 . H_2O$.
III. $[Cr(NH_3)_6](NO_3)_3$.     IV. $[Cr(NH_3)_5Cl]Cl_2$.
V. $Cr_2(SO_4)_3$ 27 per cent. basic.
VI. $Cr_2(SO_4)_3$ 40 per cent. basic.

As it is a well-known fact that chromium-cyano-complexes are so extraordinarily stable that they disintegrate only on very energetic treatment (*e.g.*, treatment with hot acids), it is not surprising that in this complex the test at 42° as well as the boiling tests show a negative result (*cf.* Table I.).

### 3.

Based on these facts as to the action on gelatin of some chromium compounds, we selected suitable chromium complex compounds for optical investigations. Anionic as well as cationic complexes were used. The choice was made from the following points of view : As the tanning compounds, as shown in preparatory experiments



FIG. 3*a*.—Absorption curves of aqueous solution of $K_3[Cr(CSN)_6]$ 0·2 per cent. vol.

I. Fresh.      II. After 3 days.
III. After 15 days.      IV. After 24 days.

are *green* (that is, of the same colour as chromium hydroxide and the basic chromium compounds) these compounds had to be selected whose light absorption process differed as much as possible from the basic
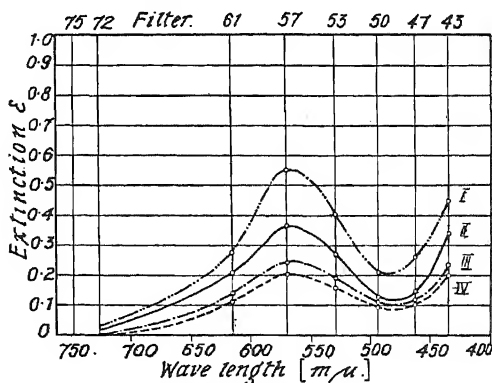
[7] E. Elöd and Th. Schachowskoy, *Collegium*, 701, 1933.

chromium compounds in order that the experiments could demonstrate even slight concentration changes of the initial compounds.    Fig. 2 shows that, for instance $[Cr(NH_3)_5Cl]Cl_2$, as well as $[Cr(NH_3)_2(CSN)_4]NH_4 . H_2O$ is far less sensitive to measurement than, for instance, $[Cr(CSN)_6]K_3$, since the situation of its absorption maximum corresponds to the position of the minimum of light absorption, e.g., of $Cr_2(SO_4)_3$ (27·7 per cent. basic), and is not disturbed by the auto light absorption of the green final product.

The light absorption conditions of the following chromium-III-compounds in water and in aqueous gelatin gels were examined :
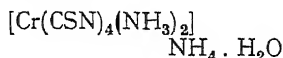
$K_3[Cr(CSN)_6]$, as an example of a compound with a tanning action, and

$[Cr(CSN)_4(NH_3)_2]NH_4$,



FIG. 3b. — Absorption curves of a solution of $K_3[Cr(CSN)_6]$ in 10 per cent. gelatin (0·2 per cent.)

| I. Fresh. | II. After 18 hours. |
| III. After 42 hours. | IV. After 66 hours. |
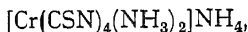
as an example of a compound with a non-tanning action.

The results can be seen in Figs. 3–4.    It will be noticed that the tanning compound *disintegrates far more rapidly in gelatin than in water*, and that on the other hand the non-tanning compound probably undergoes a change in gelatin, but that this change proceeds very slowly and moderately.    It will also be observed from    Fig. 2, that with

$[Cr(CSN)_4(NH_3)_2]$
                    $NH_4 . H_2O$

the absorption maximum is higher than the minimum of absorption of the basic chromium compounds, and this is more suitable for observation than $[Cr(CSN)_6]K_3$ whose absorption maximum is situated near the basic chromium salt.

Of the cationic chromium compounds,



FIG. 4a.—Absorption curves of aqueous solution of $[Cr(CSN)_4(NH_3)_2NH_4$ (0·2 per cent.).

| I. Fresh. | II. After 5 days. |
| III. After 10 days. | IV. After 30 days. |

$[Cr(NH_3)_5Cl]Cl_2$ was selected as a tanning representative, and $[Cr(NH_3)_6](NO_3)_3$ as a non-tanning one.    Figs. 5–7 show the results. Here, too, the same phenomena in the main may be observed ; here,
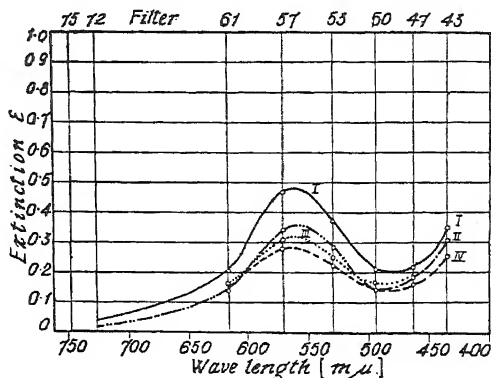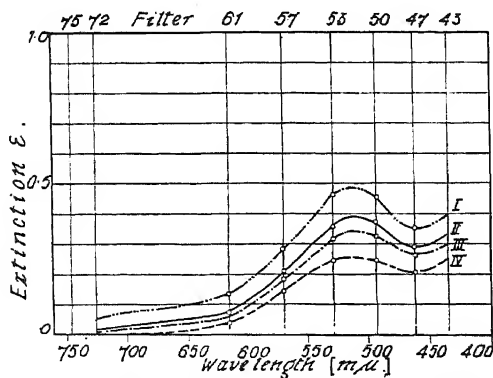
too, the tanning compound changes rapidly and clearly in the presence of gelatin ; the non-tanning complex, on the other hand, undergoes only a slight but a more rapid change in the water than the tanning compound. In the presence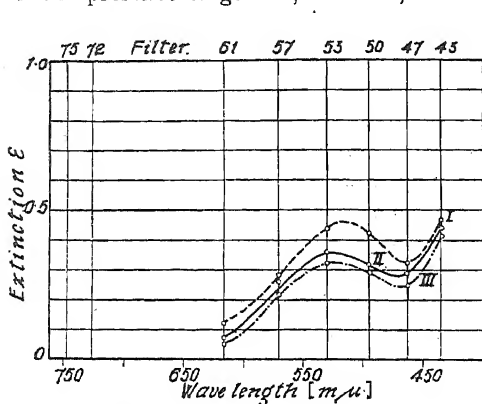 of gelatin, however, the *course* of the absorption curve had remained unchanged after eighty-eight hours, but here the conditions shown in Fig. 2 must also be taken into consideration.

In order to show how extensively the conclusions resulting from the changes of the absorption curves are connected with the action on solubility, that is, of the time required for solution, and thus with the tanning of the gelatin films, the latter were heated with the four complexes discussed above and exposed to drying processes of different durations, and the time required for solution was then ascertained as described above. From Fig. 8 we see that actually the tanning complex (used in the proportion of 2 per cent. of the gelatin dry weight) greatly increases the time required for solution of the compound after a short " ageing " process, whereas the non-tanning complex

$[Cr(NH_3)_2(CSN)_4]NH_4$
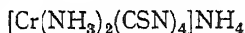
used in the same proportion (2 per cent.) causes scarcely any change in the time required for solution. Fig. 9 shows us the same picture, with the cationic complexes. The tanning complex which is difficultly soluble causes even on slight concentration of the solution a large increase of the time required for solution, whereas the non-tanning complex, even in the



FIG. 4b.—Absorption curves of aqueous solution of $[Cr(CSN)_4(NH_3)_2]NH_4$ in 10 per cent. gel. gelatin (0·2 per cent.)

I. Fresh.      II. After 45 hours.
III. After 66 hours.



FIG. 5.—Absorption curves of aqueous solution of $[Cr(NH_3)_5Cl]Cl_2$ (saturated solution).

I. Fresh.            II. After 4 days.
III. After 10 days.      IV. After 30 days.

much greater quantity of 4 per cent. of the dry weight of the gelatin, only after some time causes an increase in the time required for solution, the effect shown by $[Cr(NH_3)_5Cl]Cl_2$ is, however, by no means obtained.

The investigations of the effect of iron-III-compounds on the time required for solution of gelatin films under the afore-mentioned conditions,
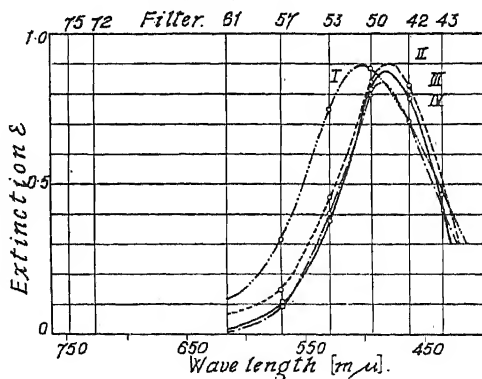
showed clearly that the tanning action depends on the stability of the compounds employed. Here, too, only the hydrolytic dissociated compounds were found to have a tanning effect (comp. Table II.).[9]

To sum up, we see by the above-mentioned experiments that the "tanning effect" in chromium-III- and iron-III-compounds depends on whether they change in the course of time in aqueous solutions or gelatin solutions or not. The change of the complexes ascertained from the course of the absorption curve runs parallel with the effect on the time required for solution of gelatin treated with the corresponding complexes. *Stable complexes have no tanning effect.*

TABLE II.—THE ACTION OF SOME IRON-III-COMPOUNDS ON GELATIN.

| Iron-III-Compounds.[8] | Behaviour of Gelatin at 42°. |
|---|---|
| $Fe(NH_4)SO_4$ | |
| $FeCl_3$ | Insol. |
| $Fe_2(SO_4)_3$ | |
| $[Fe_3(HCO_2)_6][Fe(HCO_2)_6]$ | Insol. |
| $[Fe_3(CH_3COO)_6(OH)_2]CH_3COO$ | ,, |
| $[Fe(CSN)_6]K_3$ | Not quite sol. |
| $[Fe(CN)_6]K_3$ | Sol. |
| $[Fe(CN)_5NH_3]Na_2$ | ,, |
| $[Fe(C_2O_4)_3]K_3$ | ,, |
| $[Fe_2(C_6H_4O_7)_3]H_6$ | ,, |
| Iron ammonium acetate | ,, |
| $[Fe_3(C_6H_4(OH)CO_2)_6]C_6H_4OHCO_2$ | ,, |

## 4.

There is as yet no explanation of the nature of the composition of those compounds which have a tanning effect which really arises only after a change in the complexes employed, as well as of the manner of the interaction between these compounds and the protein substance. Investigations serving to elucidate these questions were made with cobalt-III-complex compounds, the conditions of chromium-III- and iron-III-compounds being less suitable for present investigations. This is due to the facts that with the chromium - III - compounds the light sorption curves of $Cr_2(SO_4)_3$, $Cr(OH)SO_4$, etc., and of $Cr(OH)_3$ in the visible spectral range approach each other very closely (for which reason they cannot readily be separated), and that, on the other hand, conditions are complicated by the manifold character of the simple chromium compounds. The value of measurements of the light absorption in the ultra-violet are not readily evaluated, owing to the auto-light-absorption of the gelatin.
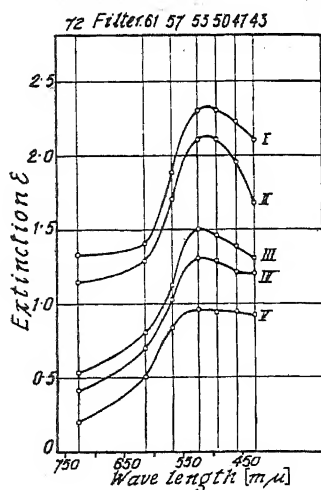


FIG. 6.—Absorption curves of a solution of $[Cr(NH_3)_5Cl]Cl_2$ in 10 per cent. gelatin.
I. Fresh.     II. After 14 hours.
III. After 42 hours.
IV. After 62 hours.
V. After 86 hours.

[8] Gmelin's *Handb. d. anorg. Chem.*, 8. Aufl. No. 59, 1932.
[9] See Lüppo-Cramer, *Koll. Z.*, **1**, 353, 1907.

## 5.

The use of cobalt-III-complex compounds for investigations of this kind offers different advantages worthy of consideration, in respect of which, as we are well aware, the application of the results to the tanning of collagen with chromium-III-compounds must not be exaggerated. Their use, however, for model experiments of the kind with which we are concerned will always stimulate and promote the clarification of our problems.
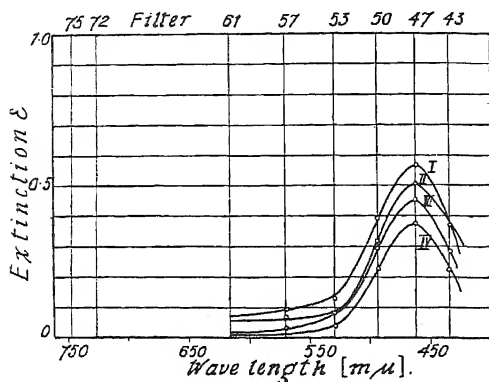


FIG. 7.—Absorption curves of aqueous solution of (0·4 per cent.) [Cr(NH₃)₆](NO₃)₃.

I. Fresh.     II. After 5 days.
III. After 10 days.     IV. After 30 days.

The cobalt-III-compounds exist in the solutions only in a complex form and as hydroxide, and this is a great advantage, having regard to the still inadequately elucidated conditions in the chromium-III-compounds. In addition, a series of well-defined cobalt-III-complexes which can be called chemically homogeneous are known from the papers on this subject of W. Biltz and R. Schwarz, among others.[10]

We have systematically examined a number of cobalt-III-complexes (altogether about 17) in regard to their action on gelatin by the method described above, and have found, in analogy with the results obtained from the chromium-III-compounds, that only those show a tanning action which were disintegrated in presence of gelatin or in aqueous solutions.

The *final stage* of such changes, as we know from the literature, being cobalt-III-hydroxide, the conditions were especially favourable, because the light absorption curves of the cobalt-III-complex compounds are all very different from those of cobalt-III-hydroxide. In this respect, the action of cobalt-III-hydroxide as a
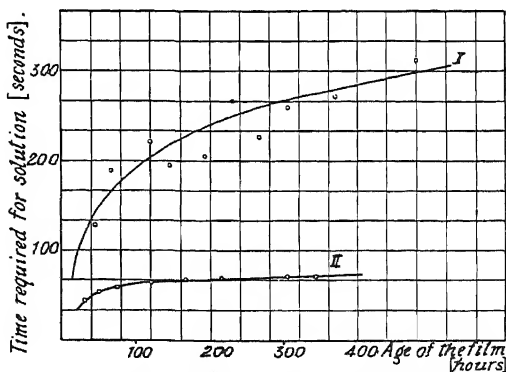


FIG. 8.—Ratio of the time required for solution of gelatin films to their age.
I. Treated with [Cr(CSN)₆]K₃.
II. Treated with [Cr(NH₃)₂(CSN)₄]NH₄ . H₂O.

[10] W. Biltz, Z. phys. chem., 67, 1909 ; 82, 561, 688, 1923 ; Z. anorg. chem. 88, 277, 1923 ; 130, 93, etc., 1923. R. Schwartz and H. Weiss, Ber., 58, 776, 1925. R. Schwarz and K. Jede, Ber., 60, 63 and 69, 1927.

tanning substance accords with the results obtained by Elöd and Sieg-mund, as well as by Meunier and by Lüppo-Cramer.[11, 12]

To illustrate the numerous investigations, let us mention as examples the conditions of light absorption when

$[Co(NH_3)_5NO_3](NO_3)_2$,

and   $[Co(C_2O_4)_3]Na_3$

(which have no tan-ning action) are used, and of

$[Co(NH_3)_3(NO_3)_3]$,

a tanning complex (*cf.* Figs. 10-12). It can be clearly seen that in the non-tanning com-pounds the change of the light absorption, if it takes place at all, is very slight in the gelatin solution, or proceeds in a different direction (*cf.* Fig. 11)[13] from tanning com-plexes, which show greater changes. It

FIG. 9.—Ratio of the time required for solution of gelatin films to their age.
I. Treated with $[Cr(NH_3)_5Cl]Cl_2$.
II. Treated with $[Cr(NH_3)_6](NO_3)_3$.

should also be observed that with $[Co(NO_2)_6]Na_3$, a tanning action could be discerned, though this must probably be considered separately, as in this case, *inter alia*, the action of the nitrous acid which is formed on decomposition can play a part.
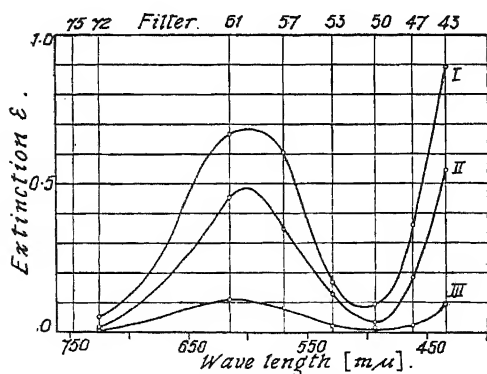
FIG. 10.—Absorption curves of aqueous solution of $[Co(C_2O_4)_3]K_3$.
I. Fresh.    II. After 3 days.    III. After 12 days.

## 6.

We must consider the following conceptions as to the nature of the in-teraction between protein and those metal com-pounds which have an actual tanning action arising during their action on the protein:

(1) Can unchanged complexes be combined with the protein? From the above evidence, this possibility must be

[11] Elöd and Siegmund, *Collegium*, 135, 1932 ; Lüppo-Cramer, *Koll. Z*, 1, 353, 1907 ; Meunier, *Le Cuir*, f. 4, 1923.
[12] E. Elöd and Th. Schachowskoy, *Collegium*, 701, 1933.
[13] The light absorption in gelatin owing to the formation of sodium oxalate and the marked sensitivity of this complex to light is difficult to ascertain quanti-tatively, but follows in the same sense as in water.

excluded at once in all the complexes investigated which have a tanning action during which they undergo changes.

(2) The formation of simple, salt-like compounds between protein and metal ions after the disintegration of the complex is improbable, since the simple salts of cobalt-III are, as we know, not very stable,[14] and rapidly change into the bi-valent, non-tanning compound. In addition, the light absorption curves in the action of tanning cobalt-III-complexes on gelatin in presence of fresh aqueous solutions, showed a change of
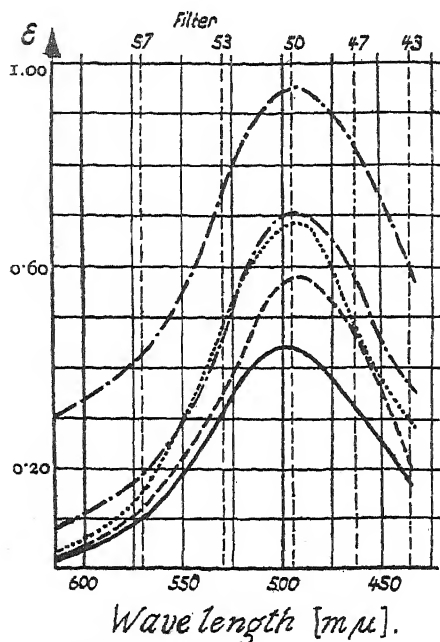
FIG. 11.—Absorption curves for solution of $[Co(NH_3)_5NO_3](NO)_2$.
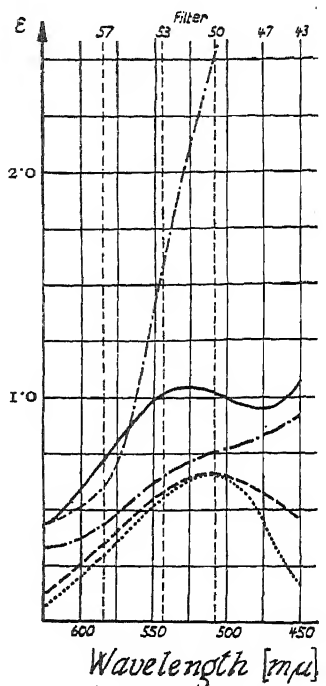
FIG. 12.—Absorption curves for solution of $[Co(NH_3)_3(NO_3)_3]$.

nature differing from that to be expected in the formation of simple cobalt-III-salts (cf. Fig. 13, curve IV.).

(3) The formation of internal complex salts between free metal ion and protein after the manner of copper glycocol is also improbable, since combinations of the latter kind, as shown in Fig. 13, cannot account for the changes of the absorption curves noticed in tanning cobalt-III-compounds. In addition, this possibility may be refused by steric-considerations, as, in the formation of internal complexes of a glycocol-

[14] i.e. E. Mischer, Helv. Phys. Acta, 3, 126, 1930.

like nature, the protein bonds may differ both in size and form, and can probably not be sterically fitted into the molecular entity (or into the entire molecule) under such mild experimental conditions (room temperature).

(4) Mixed complexes can arise in which the above-mentioned steric hindrance is less apparent. The changes of light absorption to be expected in such complexes could hardly explain the observed change.[15] However, the combination of protein on cobalt-III-hydroxide itself must not be left out of account; in this connection formal mention should be made of mixed complexes. This case will be considered below. The mainly chemical conceptions discussed under (1)-(4) thus play no further part in our considerations.

(5) During the tanning process, changes arise in the cobalt-III-complexes. The products owing to their structural nature, as shown by the papers of Debye,[16] London, and others, are able to exercise forces leading to an attachment to the protein molecule, without causing a chemical compound in the classical sense. The products of a change in initial complexes may consist of metal hydroxide or of another compound which must, however, be stable.

Since, in the tanning cobalt-III-compounds we have investigated, cobalt-III-hydroxide is formed as the final product, we have left the decision on these last two possibilities to direct experiments, but here already attention must be drawn to the fact that the absorption curves of the aqueous solutions of the cobalt-III-complexes, which have been aged for some time and in which cobalt hydroxide has formed, show far-reaching analogies with the light absorption curves measured during the action of tanning complexes on gelatin.
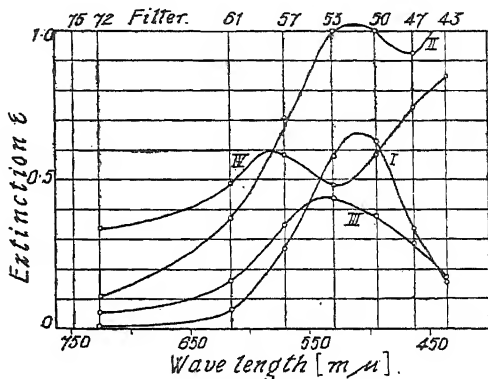


FIG. 13.—Absorption curves of

I. $[Co(NH_3)_3(NO_3)_3]$ fresh solution in water.
II. $[Co(NH_3)_2(NO_3)_3]$ in 10 per cent. gelatin (fresh).
III. $[Co(NH_2CH_2CO_2)_3]$ fresh solution in water.
IV. Co-III-Carbonate fresh solution in water.

## 7.

We therefore investigated the action of freshly-prepared cobalt hydroxide sols[17] on the solubility of gelatins. It was, however, to be expected from the outset, that the highly dispersed sols would be less active than those molecularly dispersed cobalt-III-hydroxide forming within the gelatin itself, while under the influence of cobalt-III-

[15] Cf., e.g., R. Samuel, Z. Physik, 70, 43, 1931; H. Lessheim, Jul. Meyer, and R. Samuel, Z. Physik., 43, 199, 1927.
[16] P. Debye, Physik. Z., 21, S. 178, 1920; 22, 302, 1920; Polare Molekeln, 1928; F. London, Z. Physik, 63, 245, 1930; Z. physik. Chem., 11B, 222, 1930; F. London and R. Eisenschitz, Z. Physik., 60, 491, 1930; G. Briegleb, Z. physik. Chem., 23B, 105, 1933.
[17] E. Elöd and Th. Schachowskoy, Koll. Z., 69, 205, 1934.

compounds.    With the already prepared $Co(OH)_3$ sols, part of the other-
wise effective forces are doubtless dissipated in the aggregation.



FIG. 14.—Absorption curves of aqueous $Co(OH)_3$ sols.

Experiments have shown that the cobalt-III-hydroxide sols really have a distinct action on the solubility of gelatin. Thus, the addition of 5 per cent. cobalt-III-hydroxide in the form of a sol (stabilised with 10 per cent. sodium lysalbate in proportion to the volume of the fluid) increases eightfold the time necessary for the solution of gelatin. Details of this will be published in the near future.[18]
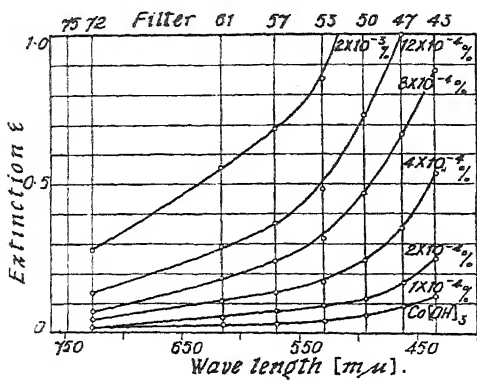
### 8.

On the other hand, it was highly important to find out whether the absorption curve of cobalt-III-hydroxide sols undergoes any changes caused by the presence of gelatin in the manner of the interaction supposed above.

Various cobalt-III-hydroxide sols with and without stabilisers were investigated by measuring their light absorption. The light absorption figures given also contain the losses of light arising in consequence of scattering of the colloidal particles.[19]

The measurements of the light absorption (Figs. 14–15) made in the colloidal solutions in the presence or absence of stabilisers showed that.[20]    Beer's law is satisfactorily fulfilled, i.e., the character of the absorption is in principle not changed by the stabilisers, and, there-fore, not by gelatin.    It is, however, possible, that by combination of hy-droxide, for instance, with gelatin the absorption *bands* of the gelatin or of the hydroxide are displaced.[21]    This effect is masked by the strong auto-absorption of cobalt-III-hydroxide.

A possible interaction between cobalt-III-hydroxide and gelatin would thus



FIG. 15.—Absorption curves of aqueous $CO(OH)_3$ sols with 2 vol. per cent. gelatin as stabiliser.

[18] E. Elöd and Th. Schachowskoy, *Kolloid Z.*, **69**, 205, 1934.

[19] *Cf.* Wien-Harms, *Handb. d. Experimentalphysik*, **19**, 388, 1928.

[20] In solutions produced in the same way, and used with the same stabilisers, in measured concentration intervals, i.e., between 0·001-0·002 per cent., $Co(OH)_3$ in aqueous solutions without stabilisers, and between 0·0015 per cent.-0·0037 per cent. $Co(OH)_3$ with stabilisators (gelatin, polyvinyl alcohol).

[21] *Cf.* J. H. de Boer, u. J. F. Casters, *Zschr. f. phys. Chem.*, **21**B, 208, 1933.

have a *different effect* on absorption from that generally to be expected in the formation of complex compounds. The same is applicable to the absorption measurements in cobalt-III-hydroxide sols in the presence of greater quantities of gelatin, as, for instance, in 10 per cent. gelatin gels containing 0·015-0·037 per cent. $Co(OH)_3$ in solution. Here, too, the light absorption of cobalt-III-hydroxide, practically unchanged in its character, could be ascertained.[22] This last evidence justifies the conclusion that even when cobalt-III-hydroxide acts on gelatin, no profound change in the cobalt-III-hydroxide takes place.

On the other hand, the fact that the solubility of gelatin becomes slighter through interaction with cobalt-III-hydroxide, indicates that changes take place in the system, in which the character of the component parts is to a greater extent preserved. The course of the absorption curve in those aqueous solutions of cobalt-III-complex bodies having a tanning action (noticed both in the presence and in absence of gelatin) leads to the conclusion that in both cases the change took place in the same sense. If, finally, we compare the absorption curves measured on pure cobalt hydroxide sols with those we have just discussed, the far-reaching analogy also existing between these two shows, that in the change of the cobalt-III-complexes possessing tanning action, both in the presence and absence of gelatin, *cobalt-III-hydroxide or a product consisting in the main of cobalt-III-hydroxide forms the final product.*

As a result of these reflections, we are justified in our conclusion that with cobalt-III-complex compounds possessing a tanning action, cobalt-III-hydroxide itself must be considered the tanning substance. It must again be emphasised that we are not justified in saying that tanning can *only* be brought about through metal-hydroxides.

## 9.

It is a known fact that the solubility of gelatin, as well as its power of swelling, decreases on tanning. The gelatin micelles consist of separate building stones (polypeptides) which, owing, probably, to the saturation of their secondary valencies, are laid together. The unsaturated part of the secondary valencies makes hydration, and consequently swelling, possible, and finally peptisation or dissolving of the gelatin. In this connection, in addition to the secondary valencies, we must bear in mind the influence of the ions both on the hydration and on the swelling capacity. The saturation of the free secondary valency parts of the micelles takes place through the dipole forces of the water molecules. It is evident that other substances possessing free forces (as, for instance, metal hydroxide or the like) can exert the rôle of the water molecules. If gelatin comes into interaction with such substances, its capacity for absorbing water decreases, as do also its swelling capacity and solubility. As the occupation of the active part of gelatin micelles by cobalt-III-hydroxide, for instance, can vary greatly as to quantity, its degree of tanning may be expected to show correspondingly different values.

The observations made here have already been discussed in another connection, viz., in the formation of molecular compounds. Stiasny, also, pointed out the part [24] played by the secondary valencies in

[22] It must be borne in mind that slight displacements of the maximum in the ultra-violet region have but little effect on that part of the absorption curve which can be easily measured. This will be more fully discussed later on.
[33] E. Stiasny, *Gerbereichemie (Chromgerbung)*, S. 533, 1931.

chromium tanning. We agree with Stiasny in this respect, but are of the opinion that for the success of the tanning it is not, as he thinks, the primary "*verolite*" or semi-colloid formations which are decisive but that it is merely the molecularly dispersed condition of the hydroxide or of the tanning compound which is of importance for the afore-mentioned saturation of the secondary valencies. Doubtless the actual interaction, for instance, between metal hydroxide and protein can be accompanied by an aggregation of hydroxide particles to greater particles. Whether we call the aggregation, in general, increase in particle size (E. Elöd), or whether we draw up a structural formula for it (E. Stiasny) is really of no importance. What, on the other hand, *is* important, is, that the inter-action itself is set up in a molecularly dispersed or at least in a mainly molecularly dispersed condition of the tanning compound.

# MEASUREMENTS OF THE DIFFUSION OF DYESTUFFS.

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*Received in German on 16th July, 1934, and translated by J. M. Rubin.*

## Introduction.

The usefulness of the numerous determinations of the diffusion co-efficients of dyestuffs is seriously impaired by the failure of earlier inves-tigators to recognise or take into account the influence of electrolytes on the diffusion velocity. Herzog and Polotzky[1] pointed out in their detailed investigation that most dyestuffs obey the diffusion laws for electrolytes and, although this has since then often been reiterated,[2, 3, 4] the influence of the electrical forces on the diffusion of dyes remained neglected. Bruins,[5] McBain and collaborators,[6] and Hartley and Robinson,[7] whose recent researches appeared independently of each other and almost simultaneously were the first to calculate the relation-ship between the rate of diffusion of a colloidal salt, the magnitude of its charge, and the concentration of the ions in the surrounding medium. They were also able to demonstrate experimentally the validity of their calculations.

It is impossible to associate the diffusion coefficient of an ion in an electrolyte solution with its molecular size or its mobility unless the con-centrations or concentration-gradients of all ions present in the solution are known. Accordingly the number of useful experiments available becomes very small, and we find that the only values obtained under sufficiently well defined conditions were the four values for pure benzidine dyes as given by Hartley and Robinson. They observed that the dif-fusion coefficient of *meta*-Benzopurpurin in the presence of an excess of salt is only one-quarter as large as that determined in pure water. For a description of the method used a reference is made to a later publica-tion which has not yet appeared. The size of the dye particles has long been recognised as an important factor in determining the behaviour of a dyestuff in the dyeing process. Since the diffusion coefficient is certainly the most reliable and easily accessible quantity for the evalua-tion of particle size we feel that the collection of suitable experimental

material on the diffusion of dyes is urgently required.   In the following
paragraphs the results obtained in our experiments to date are presented.

## Experimental.

For the diffusion measurements we chose the porous plate method
developed a few years ago by Northrop and Anson [8] and standardised by
McBain and Liu.[6a]   Though a strict mathematical understanding of the
theory underlying the method is still lacking (see Barnes,[9] Williams and
Cady [10]) its practicability has been clearly demonstrated in the investiga-
tions of McBain and Liu.   Its advantages over the other methods are :

(1) Vibration free conditions are not required.
(2) The measurements are not extremely sensitive to temperature
   fluctuations.
(3) A measurement involves only a relatively short time.

Only with respect to the last mentioned point is the microscopic method
developed by Fürth [11] and often applied
for dyestuffs [12, 13, 14] perhaps superior.
On using the porous plate, however, a
relatively large amount of solution (20-
100 c.c.) is available for the colorimetric
analysis.    Layers of liquid of 50 mm.
and more in thickness may be obtained,
whereas in the microscopic method the
thickness of the liquid layer has to be
limited to about 1 mm.    Accordingly
our measurements could be carried out
at very much lower concentrations.   This
is particularly important when dealing
with dyes very sensitive to electrolytes.

The diffusion apparatus was designed
to permit complete closing off against the
air.    This was to prevent evaporation, a
factor which becomes important when
working at elevated temperatures or
over longer periods of time, and to allow
for immersion in a thermostat.   Finally
this type of vessel makes it possible to
carry out diffusion experiments in ab-
sence of air.   These are necessary for
instance where working with the leuco
salts of vat dyes.    A sketch of the ap-
paratus which is entirely of Jena glass is
shown in Fig. 1.

A is a beaker fitted with a lid B to
which the diffusion cell is attached



FIG. 1.

The stop-cock C and the Jena glass filter are fused on to the top and bottom
of the diffusion cell.   Leading from the lid are two capillary tubes with
stop-cocks E.    These permit circulating an indifferent gas through the
apparatus, or when closed serve to make the vessel air-tight.   The ad-
justable plate F equipped with a water-level is used to adjust the horizontal
position of the filter plate.   The entire apparatus is held in position by
the ring G.   Since it is necessary that the volume of liquid in the beaker
be exactly equal to the capacity of the cell the adjustment of the level
of the liquid in beaker is carried out by means of adding small glass
spheres.   The apparatus up to the level J is immersed in a thermostat,
and held within 0·04° C. of constant temperature.

The cell constant was determined by measuring the diffusion of a stan-
dard 0·1N HCl, and taking 2·674 cm²/day as the value of its diffusion
coefficient at 25° C.
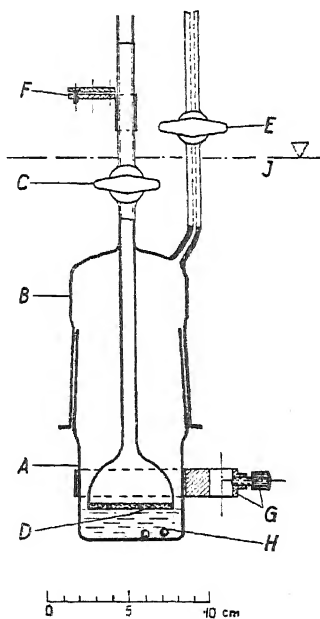
In carrying out the measurements the directions given by McBain and Liu were very carefully followed. The duration of each experiment was between twenty and seventy hours, and the quantity of diffused dyestuff between 1 and 23 per cent. of the cell contents.

A Pulfrich Stufen-photometer was used for analysing the solutions. The thickness of the layers of liquid compared did not differ by more than 30 per cent., and the salt concentrations were in all cases equal. Thus the measurements are practically independent of the validity of Beer-Lambert law.

McBain showed that in the case of molecular solutions diffusion co-efficients could be measured with an accuracy of less than 1 per cent. We confirmed this when determining our cell constant with HCl. In the experiments with dye solutions, however, we were unable to cut down the limit of error to less than 3 per cent. to 5 per cent.

## The Dyestuffs.

The diffusion of five dyes was studied : two acid wool dyes and three substantive cotton dyes

(1) **Orange II** (Schultz-Julius No. 360; Colour Index No. 151).
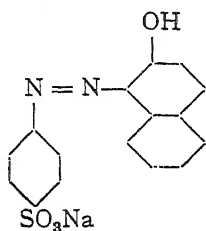


Molecular weight of dyestuff, 350.
Molecular weight of dyestuff ion, 327.

(2) **Azogrenadin S (Sorbin red)** (S.J. 105; C.I. 54).
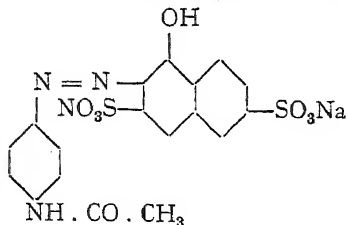


Molecular weight of dyestuff, 510.
Molecular weight of dyestuff ion, 464.

3) **Benzopurpurin 4B** (S.J. 448 ; C.I. 448.)
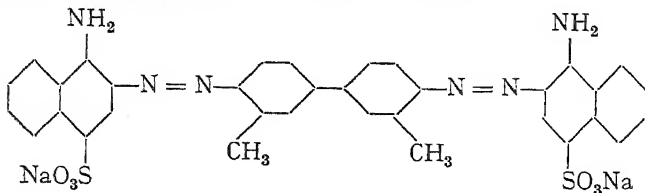


Molecular weight of dyestuff, 724.
Molecular weight of dyestuff ion, 678.

(4) **Congo red** (S.J. 360 ; C.I. 370).
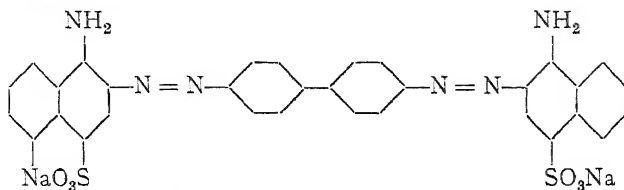


Molecular weight of dyestuff, 696
Molecular weight of dyestuff ion, 652.

(5) **Chicago Blue 6B** (S.J. 511 ; C.I. 518).
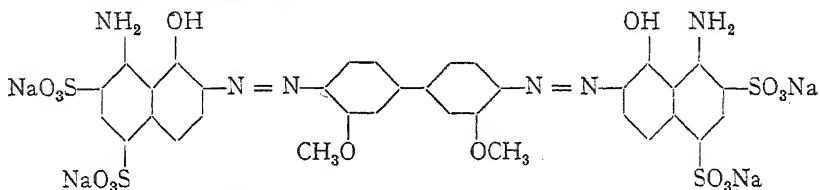


Molecular weight of dyestuff, 992
Molecular weight of dyestuff ion, 900

Benzopurpurin and Congo Red were selected because they had already been the subject of numerous physico-chemical investigations.[16-21] Chicago Blue as well as the other two benzidine dyes figured in the important experiments of Neale [22] on the mechanism of cotton dyeing, and were included for that reason.

The dyes with the exception of those used in experiments listed in Table III. were all carefully purified. Orange II. was recrystallised several times from pure water. The other dyes were purified according to the method of Robinson and Mills [19] by precipitating repeatedly from water containing an excess of sodium acetate, and then freeing of salt by washing with alcohol. The purity of the products was controlled by analysis and by examining the electrical conductivity of their solutions.

The specific conductivity of the water used in this

TABLE I.—DIFFUSION COEFFICIENTS OF DYESTUFFS IN PURE WATER.

| Dyestuff. | Weight Concentration (in per cent.). | $D_{25}°$ of the Dyestuff Ion in $cm^2/day$. |
|---|---|---|
| Orange II . . | 0·1 | 0·690 |
| ,, . . | 0·5 | 0·644 |
| ,, . . | 1·56 | 0·577 |
| Azogrenadin S . | 0·05 | 0·655 |
| ,, . | 0·1 | 0·679 |
| ,, . | 0·5 | 0·638 |
| Benzopurpurin 4B | 0·02 | 0·624 * |
| ,, . | 0·025 | 0·646 * |
| ,, . | 0·1 | 0·590 |
| ,, . | 0·2 | 0·617 |
| ,, . | 0·5 | 0·529 |
| Congo red . . | 0·01 | 0·659 * |
| ,, . . | 0·03 | 0·666 |
| ,, . . | 0·03 | 0·670 |
| ,, . . | 0·1 . | 0·610 |
| ,, . . | 0·1 | 0·622 |
| ,, . . | 0·5 | 0·573 |
| Chicago blue 6B . | 0·05 | 0·605 |
| ,, . . | 0·1 | 0·626 |
| ,, . . | 0·5 | 0·528 |

\* These values are somewhat uncertain, since the conductivity of the water could no longer be neglected in comparison with that of the dye salt solution.

8 *

investigation varied between 2 and $3 \times 10^{-6}$ $\Omega^{-1}$. The sodium chloride was a Merck product (puris).

## Experimental Results.

Experiments were carried out in pure water and in NaCl solutions. In the latter case the salt concentrations both in the cell and in the surrounding medium were the same. (See Tables I. and II.)

For the sake of comparison some measurements were made on the unpurified commercial dye products (see Table III.).

TABLE II.—DIFFUSION COEFFICIENTS OF DYESTUFFS IN NaCl SOLUTION.

| Dyestuff. | Weight Concentration (in per cent.) | Concentration of NaCl in Mol. | $D_{25}°$ of Dyestuff Ions in cm²/day. |
|---|---|---|---|
| Orange II . . | 0·005 | 0·02 | 0·444 |
| ,, . | 0·01 | 0·02 | 0·444 |
| ,, . | 0·02 | 0·05 | 0·400 |
| ,, . | 0·02 | 0·2 | 0·393 |
| ,, . | 0·05 | 0·2 | 0·353 |
| Azogrenadin S . | 0·005 | 0·05 | 0·405 |
| ,, . | 0·01 | 0·02 | 0·404 |
| ,, . | 0·01 | 0·05 | 0·425 |
| ,, . | 0·01 | 0·05 | 0·424 |
| ,, . | 0·02 | 0·02 | 0·425 |
| ,, . | 0·05 | 0·05 | 0·399 |
| ,, . | 0·01 | 0·1 | 0·375 |
| ,, . | 0·1 | 0·1 | 0·330 |
| Benzopurpurin 4B | 0·005 | 0·01 | 0·228 |
| ,, . | 0·01 | 0·01 | 0·205 |
| ,, . | 0·01 | 0·01 | 0·215 |
| ,, . | 0·002 | 0·02 | 0·206 |
| ,, . | 0·005 | 0·02 | 0·188 |
| ,, . | 0·005 | 0·02 | 0·180 |
| ,, . | 0·01 | 0·02 | 0·187 |
| ,, . | 0·02 | 0·02 | 0·187 |
| ,, . | 0·03 | 0·03 | (0·092)* |
| ,, . | 0·02 | 0·05 | (0·052)* |
| ,, . | 0·05 | 0·05 | (0·038)* |
| Congo red . . | 0·005 | 0·02 | 0·166 |
| ,, . | 0·01 | 0·02 | 0·165 |
| ,, . | 0·01 | 0·05 | 0·161 |
| ,, . | 0·02 | 0·05 | 0·149 |
| ,, . | 0·05 | 0·1 | 0·134 |
| ,, . | 0·05 | 0·1 | 0·135 |
| ,, . | 0·05 | 0·2 | (0·106)* |
| Chicago blue 6B . | 0·002 | 0·01 | 0·244 |
| ,, . | 0·005 | 0·02 | 0·235 |
| ,, . | 0·02 | 0·02 | 0·212 |
| ,, . | 0·02 | 0·05 | 0·205 |
| ,, . | 0·02 | 0·1 | 0·184 |
| ,, . | 0·02 | 0·2 | 0·136 |
| ,, . | 0·02 | 0·5 | 0·121 |
| ,, . | 0·2 | 0·5 | 0·102 |

\* Precipitation during the experiment.

## Discussion of the Results.

The diffusion of electrolytes has lately been the subject of numerous theoretical investigations. The generalisation of the Nernst equation for the case of polyvalent ions, the influence of the corresponding and oppositely charged ions, and the influence of the ionic atmospheres have been extensively discussed. In the following we shall briefly review the principal results of these theoretical researches.

The diffusion coefficient of an electrolyte in an infinitely dilute solution is determined by the mobilities of the two ions [23, 25, 3-7]

$$D = \frac{RT}{F^2} \times 10^{-7}\left(\frac{1}{n_+} + \frac{1}{n_-}\right)\frac{u \times v}{u + v} \qquad . \qquad . \qquad (1)$$

$n_+$ and $n_-$ : valence of the anion and cation ; $u$ and $v$ : their equivalent mobilities in $\Omega^{-1}$. The diffusion coefficient of a (negative) ion in an aqueous solution which in addition to the corresponding opposite ion also contains a homogeneously distributed foreign electrolyte is given by a function of the mobility of each ion present and the concentrations of both electrolytes [24-27]

$$D = \frac{RT}{F^2} \times 10^{-7} \frac{v}{n_-} \left[ 1 - n_- \frac{\dfrac{v}{n_-} - \dfrac{u}{n_+}}{u + v + \dfrac{c'}{c}(u' + v')} \right]. \qquad . \quad (2)$$

$c$ : the equivalent concentration of the electrolyte containing the anion whose diffusion coefficient is to be computed. $u$, $v$, $n_+$ and $n$ have the same significance as above.

$c'$ : equivalent concentration of the homogeneously distributed foreign electrolyte ; $u'$ and $v'$ : mobilities of the respective cation and anion.

TABLE III.—DIFFUSION COEFFICIENTS OF UNPURIFIED DYESTUFFS IN NaCl SOLUTION.

| Dyestuff. | Weight Concentration (in per cent.). | Concentration of NaCl in Mol. | $D_{25^\circ}$ of Dyestuff Ions in cm²/day. |
|---|---|---|---|
| Benzopurpurin 4B | 0·02 | 0·02 | 0·190 |
| Congo red  .     .  | 0·05 | 0·05 | 0·168 |
| Chicago blue 6B  . | 0·05 | 0·05 | 0·231 |
| ,, | 0·1 | 0·1 | 0·216 |

In the presence of an excess of a foreign electrolyte $(c' \gg c)$ the diffusion coefficient of a (negative) ion is dependent on its mobility alone : [24, 5, 7]

$$D = \frac{RT}{F^2} \times 10^{-7} \frac{v}{n} \qquad . \qquad . \qquad . \qquad . \quad (3a)$$

or

$$D = \frac{kT}{6\pi\eta r} \qquad . \qquad . \qquad . \qquad . \qquad . \quad (3b)$$

($k$ : Boltzmann constant $= RT/N$ ; $r$ : radius of the anion
            $\eta$ : viscosity of the solvent).

Expressing the diffusion coefficient in cm.²/day instead of cm²/sec. we have 0·0229 for the value of the constant $\dfrac{RT}{F^2} \times 10^{-7}$ at 25°.

The above relations, however, are valid only for infinitely dilute solutions, and do not apply to real solutions where the effect of the distribution of the ions must also be considered. The modern theory of electrolytes has succeeded in accounting for the deviations of an electrolyte solution from its ideal behaviour up to a concentration of about 0·01 $N$. The problem of diffusion of electrolytes in real solutions has also been extensively dealt with. (McBain and Liu,[6a] Hartley,[25] Bruins,[5] Sitte,[26] Onsager and Fuoss.[27] The last named paper is perhaps the most thorough and the most exact.) On the other hand, however, it has been found that the behaviour of colloids cannot in general be quantitatively described by the derived relationships. This is due to the extreme asymmetry of charge and particle size between the anion and cation of a colloidal salt ; the charge of the extraordinarily large and high valent colloidal

ion is compensated by the small monovalent oppositely charged ions.[4, 28] In some cases, however, the size of the colloid ion is sufficiently large to compensate the effect of its high valence. Such a colloidal salt behaves like a low valent electrolyte (for instance soaps, compare McBain[29]). In our present state of knowledge it is impossible to decide whether this is also true for dyestuffs. Nevertheless two different effects of the ion distributions on diffusion are distinguishable :

Firstly the driving force (*i.e.* in case of dilute solutions, the concentration gradient) is lowered. This effect is expressed by the factor $\left( 1 + c \dfrac{d \log f}{dc} \right)$ where $c$ is the concentration and $f$ the activity coefficient. And secondly the frictional resistance is subject to the influence of the ionic orientation. This is of lesser importance for diffusion than for the case of electrical conductivity. An electrical current moves the cations and anions in opposite directions ; the forces of diffusion in the same direction. In the latter case the velocity of both ions of a binary electrolyte will be equal and the ionic atmospheres will thus undergo no deformation. The electrophoretic resistance does not only become very small, but under certain conditions the hydrodynamic forces set up by the uniformly directed motion of the ions can actually cause a decrease of the frictional resistance below that calculated for an infinitely dilute solution. In mixtures of electrolytes containing ions of different diffusion velocities the situation is much more complicated.

The experimental results presented in Table I. may be better understood if we first consider the three cases typical for the diffusion of dyes :

(*a*) *The dye is a sodium salt of an unassociated monobasic acid of high molecular weight.*

Assuming 20 $\Omega^{-1}$ as the mobility of the anion in an infinitely dilute solution at 25° (compare Wegscheider's data in the compilation of Lorenz[30]). The Nernst equation (Equation 1) becomes

$$D = 0\cdot0229 \times 2 \times \frac{50 \times 20}{50 + 20} = 0\cdot657 \text{ cm.}^2/\text{day.}$$

Up to a concentration of about 0·1 $N$ the interionic forces cause a decrease of this value which is approximately linear with respect to the square root of the concentration. This effect, due principally to a diminishing of the " driving force," rarely exceeds 10 per cent. even in a 0·1 $N$ solution.

(*b*) *The dye is a sodium salt of an unassociated dibasic acid of high molecular weight.*

In this case 35 $\Omega^{-1}$ can be taken as the mobility of the anion, and using the generalised Nernst equation (Equation 2) we have

$$D = 0\cdot0229 \times 1\cdot5 \times \frac{35 \times 50}{35 + 50} = 0\cdot710 \text{ cm.}^2/\text{day.}$$

The value of $D$ decreases more rapidly on increasing the concentration then in case (*a*).

(*c*) *The dye is a sodium salt of a completely dissociated acid whose anions are strongly aggregated.*

Taking 60 $\Omega^{-1}$ as the equivalent mobility of the anions in infinitely dilute solution and using the generalised Nernst equation we have since $1/n \ll 1$

$$D = 0\cdot0229 \times 1 \times \frac{60 \times 50}{60 + 50} = 0\cdot627 \text{ cm.}^2/\text{day.}$$

If the anions are only slightly aggregated, the above value must be multiplied by $\left(1 + \dfrac{1}{n}\right)$ where $n$ is the valence of anionic aggregate. The aggregation of five divalent dyestuff ions to one micelle would give a factor $1\cdot 1$ and the value of the diffusion coefficient would increase to $0\cdot 690$ cm$^2$/day. Owing to higher valence of the anion the influence of the interionic forces would be considerably greater than in the two previous cases.

This discussion would not be complete without considering the effect of ionic association or, respectively, incomplete dissociation. In case $(a)$ the value of the diffusion coefficient of a dyestuff dissociating only to 50 per cent. would decrease to $0\cdot 4$ cm.$^2$/day. In case $(b)$ the diffusion coefficient of a 50 per cent. dissociated salt would be $0\cdot 66$ cm.$^2$/day, the system practically reverting to case $(a)$. Finally in case $(c)$ the diffusion coefficient will remain independent of the degree of dissociation as long as the equivalent mobility of the anion is not decreased. If this occurs the value for the mobility of the anion must be replaced by the one the anion aggregate of diminished valence would possess at infinite dilution.

From the above we can conclude that each of the three cases discussed leads to the approximatively same values for the diffusion coefficient. Thus, this quantity alone can yield us no information on the degree of aggregation of a pure dyestuff (compare also Hartley and Robinson[7]). Only after a comparison with the diffusion coefficient obtained in salt solution, were we in a position to conclude that the anions of Orange II. (case $(a)$) and Azogrenadin S (case $(b)$) are practically unassociated in the investigated concentration range, while Benzopurpurin 4B, Congo Red, and Chicago Blue 6B associate to form micelles (case $(c)$).

The assumption made above that the equivalent mobility of the non-aggregated anion is smaller than that of the aggregated ion is, as can be seen from the results of the diffusion experiment, entirely justified. The value of $0\cdot 4$ cm.$^2$/day for the diffusion coefficient of the wool dye anion in excess salt solution indicates a mobility of $18\Omega^{-1}$ for a monovalent ion or $36\Omega^{-1}$ for a divalent. The high values assumed for the mobility of the aggregated anions is supported by Robinson and Moilliet's [21] determinations of the transport numbers and conductivities of Benzopurpurin 4B. Their experiments indicate a value for the equivalent mobility of the anion which increases with the dilution up to $54\cdot 9\Omega^{-1}$ in a $0\cdot 02$ per cent. solution. This value, however, also includes the braking-effect of the ionic atmospheres, which as mentioned above fully disappears in the case of diffusion.

Before considering the results contained in Table II. it is first necessary to make certain that the applied salt concentrations were high enough in solution to the dyestuff concentration to prevent the occurrence of a diffusion potential on the interface, and thus allow the use of equation 3 for measuring the diffusion coefficient under conditions independent of the electrical forces. It was estimated that the dyestuff contributed at the maximum only 2 per cent. to 3 per cent. to the conductivity of the solution, and in most cases only a small fraction of this value. However, as the diffusion coefficient is dependent on the dyestuff concentration as well as on the salt concentration it is impossible strictly to prove that the excess of salt was large enough. That this is highly probable may be seen on inspecting the results obtained. Especially convincing is the fact that on manifoldly increasing the dyestuff concentration for the same concentration of salts the diffusion coefficient often decreases, but that it never increases above the limit of the experimental error.

The values in Table II. can thus be used for calculating the radius of the particles according to the Stokes-Sutherland-Einstein formula: $D = \dfrac{kT}{6\pi\eta r}$. Using the value of the viscosity of pure water for $\eta$ and expressing $D$ in cm.$^2$/day we have (for 25°) $r = \dfrac{2 \cdot 10 \cdot 10^{-8}}{D}$ cm.

Gans [32] and Herzog and Kudar [31] have shown that the error involved in assuming spherical form for comparatively small particles such as here dealt with is relatively small, except of course in cases of extreme anisodiametrical systems such as chains, etc. Thus, using the macroscopic specific weight (1·5) and neglecting the hydration we are in a position to calculate the weight of a particle. In the last column of Table IV. the aggregation numbers (i.e. the number of dyestuff ions contained in each particle) are given.

TABLE IV.

| Dyestuff. | Weight Concentration of Dyestuffs (in per cent.). | Concentration of NaCl in Mol. | D in cm²/day (mean values). | r in 10⁻⁸ cm. | Mol. Weight of Particles. | Aggregation No. |
|---|---|---|---|---|---|---|
| Orange II . | 0·005-0·01 | 0·02 | 0·44 | 4·77 | 413 | 1·2 |
| Azogrenadin S . | 0·005-0·05 | 0·02-0·05 | 0·41 | 5·12 | 511 | 1·1 |
| Benzopurpurin 4B | 0·002-0·01 | 0·01-0·02 | 0·21 | 10·0 | 3810 | 5·6 |
| ,, | 0·005-0·02 | 0·02 | 0·18 | 11·7 | 6100 | 9·0 |
| Congo red . | 0·005-0·01 | 0·02-0·05 | 0·16 | 13·1 | 8560 | 12 |
| ,, . . | 0·05 | 0·1 | 0·13 | 16·2 | 16200 | 24 |
| Chicago blue 6B . | 0·002-0·02 | 0·02-0·05 | 0·22 | 9·55 | 3310 | 3·7 |
| ,, . . | 0·02 | 0·1 | 0·18 | 11·7 | 6100 | 6·8 |
| ,, . . | 0·02 | 0·2 | 0·14 | 15·0 | 12800 | 14 |
| ,, . . | 0·02 | 0·5 | 0·12 | 17·5 | 20400 | 23 |

Orange II. and Azogrenadin S, under the conditions investigated, are molecularly dispersed. Benzopurpurin 4B shows a tendency to aggregate which increases on raising the electrolyte concentration; however, owing to the electrolyte sensitivity of this system it was impossible to determine the aggregation number in NaCl solutions more concentrated than 0·02 $N$. At this concentration an aggregation number of 9 for a 0·02 per cent. solution was obtained. Chicago Blue 6B and Congo Red in 0·05 $N$ salt solutions contain aggregates of 12 and 4 dyestuff anions respectively. The aggregation numbers increase very rapidly on any further raising of the salt concentration.

It should be stressed that the influence of the interionic forces on the activity and frictional resistance of the dyestuff anion have been neglected in the calculations of particle size.

## Comparison with Previously Published Results.

Of all the diffusion values previously published only those obtained by Robinson for dyestuffs in pure solutions are comparable with the data presented here. His values calculated for 25° are 0·61 cm.$^2$/day for a 0·03 per cent. Congo Red solution and 0·48 cm.$^2$/day for a Benzopurpurin 4B solution of the same concentration. As noted by Hartley and Robinson [7] this value for Benzopurpurin 4B is below their theoretically calculated minimum value. They attribute this discrepancy

to the presence of impurities.   Their value for Congo Red is also some-what lower than ours.

Comparing the diffusion coefficient of the technical and purified dyestuffs (Tables III. and II respectively), in equally concentrated salt solutions it is seen that the results obtained are approximately the same.   This is important for the technical application of this method, but does not imply that the results of all the previously determined diffusion coefficients of dyestuffs are correct.   With few exceptions [14] the diffusion coefficients were not determined in an excess of salt homo-geneously distributed throughout the whole system, but rather the dyestuff was dissolved in a salt solution and diffused against pure water. Hartley and Robinson pointed out that the values obtained in the above experiments would be dependent on the mobility and concentration of the ionic impurity and further would vary with the different methods of measurement.   Having regard to this the divergence between the previously published data is not at all surprising.   The diffusion co-efficients of Congo Red (converted to $25°$) are, for example, as follows :

Herzog and Polotzky [1] :   $0·1—0·15$ cm.$^2$/day (conc. 2·5 per cent.)
Fürth and Ullmann [11b] : $0·16—0·18$    ,,   ( ,, $<0·12—0·06$ per cent.)
Ostwald and Quast [33] :   $0·08—0·12$    ,,   ( ,, $<0·02$ per cent.)
     purified
Nistler [12] :                $0·12—0·14$    ,,   ( ,, $<0·125—0·002$ per cent.)
Brass and Eisner [34] :   $0·08$            ,,   ( ,, $0·1$ per cent.)

Ostwald and Quast used purified dyestuffs, yet their value for Congo Red is still very low.   Brass and Eisner also using a purified Congo Red determined its diffusion coefficient at $0·4$ cm.$^2$/day.   This value is in fair agreement with the results obtained by Robinson, and roughly agrees with our value for the diffusion coefficient against pure water.   The dif-fusion coefficients as determined by Brass and Eisner for a number of purified and impure dyestuffs illustrate clearly the effect of the electrical forces on the diffusion velocity.   Their values for the purified dyes are consistently many times greater (up to twenty-fold) than those for impure dyes.   Brass and Eisner conclude that the particle size of the purified dyes is very much smaller than that of the unpurified.   In reality the difference in the diffusion coefficient is undoubtedly a result of the differences between the effective diffusion potentials.

Herzog and Polotzky were unable to observe any diffusion of Benzo-purpurin 4B.   This was probably due to salt impurities present in suffi-cient quantity to flocculate the dyestuff.   Ostwald and Quast found a diffusion coefficient of $0·06$-$0·09$ cm.$^2$/day for a $0·02$ per cent. solution of purified Benzopurpurin 4B against pure water.

## Particle Size, Aggregation, and the Dyeing Process.

We can conclude from our diffusion measurements that the acid dye-stuffs investigated are molecularly dispersed and we have confirmed the assumption already made on the basis of their behaviour on osmosis and dialysis and of their electrical conductivity, that the substantive cotton dyes are aggregated to ionic micelles.   The calculated aggregation number of Benzopurpurin 4B is much smaller than that generally as-sumed.[21]   However a closer inspection of the experimental data on the osmotic behaviour of dyes and on their electrical conductivities and transport numbers show that these are not necessarily in contradiction with the above determined aggregation numbers.   This is also true for

Congo Red (it is well known that Congo Red as result of its *zwitterionic* nature is more highly aggregated in acid solution (compare Pauli and Weiss [35])).

We have also been able to observe the long assumed fact that the aggregation increases on raising the salt concentration. On the other hand, however, we have not observed a maximum in the relation between the diffusion coefficient and the salt concentration, as has occasionally been reported.[14]

The aggregation numbers derived from the diffusion measurements in excess salt solutions enable us to draw certain conclusions about the size of the molecules in pure solution. It can be assumed with some certainty that the aggregation in a pure solution at a given dyestuff concentration is always smaller than in a salt solution. On concentrating the dye solution an increased aggregation must be expected for two reasons : firstly the law of mass action requires a displacement of the equilibrium ; secondly the increased number of ions from the dissociating dyestuff give rise to a salt effect. This effect is generally smaller than that of a monovalent salt of the equivalent concentration. The magnitude of the first effect may be estimated from the values of the diffusion coefficient determined in solutions of different dye content.

Owing to the technical importance of adding salt to the dyeing baths, by which the substantivity of the dyestuff is enhanced, the influence of salts on dyes is of special interest. According to the particle size theory [36] the effect of adding salt is the establishing of a degree of dispersion suitable for the dyeing process. That an addition of salt diminishes the degree of dispersion can be accepted as clearly proved by our diffusion experiments. We do not however believe that this necessarily supports the dispersion theory of dyeing. We are rather of the opinion that the symbatic behaviour of the aggregation and of affinity may in both cases be traced back to the same cause, and that it is unnecessary to assume any direct causal relationship between the two.

The relationship between the observed influence of salts on the dye absorbtion equilibrium and the value of the diffusion coefficient has been well stated by Boulton, Delph, Fothergill and Morton : [37]

" The affinity of the dyestuff for the water-phase can be reduced by the addition of salt, as is shown by the general development of colloidal properties when salts are added to solutions of direct dyes. The presence of salt in the absorption system therefore favours an equilibrium displaced to give an increased amount of dye on the fibre."

The " development of colloidal properties " is most clearly revealed in the aggregation.

In the course of the last few decades various theories of the mechanism of the dyeing process have been proposed, yet really careful investigations on the subject of cotton dyeing have appeared only very recently.[23, 27] The absolutely necessary clear distinction between the kinetics of the process and the determination of the equilibrium was first observed in the above cited investigations. The kinetics of the process are determined by the rapid establishing of a stationary equilibrium on the outer surface of the fibre, and by a slow diffusion of the absorbed dye into the interior. The dyeing process is complete and the real equilibrium is reached when the dye is uniformly absorbed throughout the bulk of the fibre. The influence of salt on this equilibrium is in all cases very simple : the amount of absorbed dye increases with an increasing salt concentration. The

apparent diffusion constant, however, which defines the rate of absorption of a dyestuff by a cellulosic material varied, according to Neale and his co-workers,[22] in a complex manner with the salt concentration. This, they explain, is due to the influence of the affinity on the apparent diffusion constants. They also show that the application of Hill's [38] equation (which was simultaneously developed by March and Weaver [39]) is permissible, and that it suffices for a description of their experimental material. The mechanism of the process, however, is in our opinion more correctly expressed by the equations developed by Hill in the fourth part of his paper. It must be considered, that the dye on penetrating into the fibre becomes partially fixed—at least, if we assume that the dyeing process is a unimolecular adsorption of the dyestuff at the interfaces of the water-filled spaces in the cellulose material.[40,41] This circumstance makes it impossible to compare directly the diffusion constants measured in cellophane and in pure soluton.

It is very doubtful that the colouring substrate consists of aggregate of colloidal ions or salts as proposed by Haller's [36] dispersion-degree theory. From the investigation of Adam,[42] Rideal,[43] Gorter and Grendel,[44] Katz,[45] and others, we know that not only liquids but also solid substances may spread out into mono-molecular layers on surfaces. Further, it has observed that molecules whose diffusion coefficients suggest a particle diameter of 5 m$\mu$, and more may form layers 0·7 m$\mu$ in thickness. It is therefore not at all improbable that the loosely formed dyestuff micelles are dispersed under the influence of the surface forces of the cellulose into single molecules, forming a mono-molecular layer. It is also conceivable that the dyestuff penetrates into the fibre by way of a " diffusion in the adsorbed phase " as is well known in the case of the solid-vapour interface.[46, 47, 48] Unfortunately, we know of no method by which we can experimentally investigate this problem. If this conception is true the Neale diffusion coefficients would represent the actual diffusion coefficient of the adsorbed dye molecules, multiplied by an unknown but constant factor accounting for the dimensions of the inner surfaces of the fibre. Finally, we must consider that the aggregation number merely represents an average value over all the particles present in the association equilibrium, and that perhaps it is only the unassociated molecules that take part in the dyeing process.

The effect of salts on micelle formation in solutions of soaps and wetting and emulsifying agents is analogous to that in dye solutions. The tendency to form ionic micelles is an expression of a certain spacial asymmetry of the hydrophylic and cohesive forces of the molecule. This molecular force-asymmetry is responsible for the surface and interface activity of these technically important substances. Soaps, for instance, are generally used at such high dilutions that neither neutral colloids nor ionic micelles are present in the solution. The formation of these association products occurs only on lowering the temperature or increasing the concentration. The enhancing of the surface and interface activity of soaps, wetting agents, and emulsifying agents by adding salts to their solutions is fundamentally the same phenomenon as the increasing, by salt addition, of the amount of dyestuff accumulated on the inner surfaces of the cellulose material.

For a further study of the relationships between the diffusion coefficients and the technical behaviour of dyestuffs, it will be necessary to carry out diffusion measurements at the elevated temperatures actually encountered in the dyeing process. As the solubility of dyes generally increases rapidly on raising the temperature, a considerably smaller aggregation is to be expected. Benzopurpurin 4B at room temperature

is coagulated in a 0·03 $N$ NaCl solution.  At its boiling temperature such a solution is perfectly clear, even if the NaCl concentration be raised to 0·1 $N$.  For these reasons we have already undertaken a series of measurements on the diffusion coefficients of dyes at elevated temperatures.

### Relations between Mobility, Valence and Diffusion Coefficient of Colloidal Ions.

A direct relationship between the three quantities $v$, $n_-$, and $D$ is given by equation (3a).  For ordinary electrolytes this equation can be confirmed by comparison with the generalised Nernst diffusion equation (Eqn. 1).  Also, as is shown above, the diffusion coefficients of Benzopurpurin 4B and Congo Red in pure water can be correctly expressed by equation (3a).  The values for the aggregation numbers in Table III. can be used to calculate the valence of the anion complex.  This quantity together with the experimentally determined diffusion coefficient, substituted in equation (3a), $v = \dfrac{Dn_-}{0 \cdot 0229}$, yields a calculated value for the equivalent mobility which may be compared with the experimental value.  For Benzopurpurin 4B in diluted solution we have

$$v_{25°} = \frac{0 \cdot 21 \times 11}{0 \cdot 0229} = 100 \ \Omega^{-1}.$$

Yet in a 0·02 per cent. sol. the electric mobility of the dyestuff ion is 54 $\Omega^{-1}$, and that of opposite sodium ion 43 $\Omega^{-1}$.  This means that while mobility of the Na ions was only 14 per cent. less than at infinite dilution, the mobility of the anion as measured electrolytically was 44 per cent. less than the mobility calculated from the diffusion coefficient measured in an excess of salt.  (In the case of incomplete dissociation the decrease of gegenion mobility can be very much less than 14 per cent.)  On the other hand, if we substitute this value of 100 $\Omega^{-1}$ in equation (1) a diffusion coefficient of 0·84 cm.$^2$/day instead of the experimentally determined 0·65 cm.$^2$/day would be obtained.  It dealt with the same phenomenon, which Robinson and Moilliet[21] describe as the fact that the application of the Einstein-Stokes law to the experimentally determined electrical mobility of Benzopurpurin 4B results in the improbably low aggregation number of only 1·5.  In accordance with these authors we can assume that the interionic forces are responsible for the discrepancy and we can express it by the statement that the *conductivity coefficient of the colloid ion is considerably smaller than that of the gegenion.*  The hydration of the micelles could also be considered partly responsible for these deviations.

On the other hand, it appears that this is a general effect, which becomes more important as the particle size and particle charge increases.  The best example of this anomaly is the case of egg albumin in hydrochloric acid solution.  It was through this example that Pauli and I demonstrated it in 1926,[49] and since then have often mentioned it.[4, 50]  Nevertheless, since many new important contributions have been made to the subject since then, I would like to review it in brief.

Starting with an iso-electric egg albumin, we find that, on increasing the hydrogen-ion concentration, increasing quantities of protons are taken up.  The valency of the heavy cation increases till a saturation point is reached.  At this concentration about 1 mol. of $H^+$ is taken up for every 1100-1200 g. of protein present.  Assuming a molecular weight

of 34,500 for the egg albumin, we find that this is equivalent to about 30 positive charges for each protein molecule. A measurement of the mobility of the egg albumin yields at the maximum, a value of 30 $\Omega^{-1}$, which, according to Stokes' law, indicates only 6 charges per particle. The mobility of the colloid ion appears, therefore, to have been reduced to 20 per cent. On the basis of activity and conductivity measurements the conductivity coefficient of the opposite ion ($Cl^-$) cannot be considered smaller than 0·6. This deviation is still more marked in the case of serum albumin, which is twice as large as egg albumin, and is 60-valent.

McBain, Dawson, and Barker,[6e] in a recent investigation on the diffusion of albumin in hydrochloric acid solutions, found on applying the general diffusion equation a maximum of 6 charges on each protein cation· They attribute the difference between this value and that of 21 free charges found by Pauli, Frisch, and Valkó [51] to the presence of unknown impurities in their diffusion experiments. However, in view of the low conductivity of their protein solutions, and the relatively high concentration of salt present taken into account by them, this explanation seems somewhat improbable, and especially so since their value agrees so well with that calculated from the experimentally observed mobilities. Thus the colloid ion of egg albumin, just as was the case for Benzopurpurin 4B, encounters a much greater frictional resistance on diffusing under the influence of an electric force than when freely diffusing. This increased frictional resistance is approximately equal to the resistance met on current transport. Though it is possible in the case of the electrolytic mobility that the asymmetry of the ionic atmospheres might be made responsible for the above, the behaviour on diffusion clearly shows that of all the interionic braking forces this one cannot account for the deviation. We therefore believe it necessary that a clear distinction be made between the frictional resistance in " osmotic " or " neutral " diffusion which results solely from a concentration (activity) gradient, and that in electrical diffusion under the influence of a diffusion potential.

Reviewing the different equations for the diffusion of electrolytes from this point of view we reach the following conclusions:

For ordinary electrolytes the two frictional resistances are equal. This is confirmed by the validity of the Nernst equation.

For high valent colloid ions diffusing in pure water the electrical diffusion entirely outweighs the " neutral " diffusion, and the diffusion coefficients obtained corresponds to the electrical frictional resistance.

For high valent colloid ions diffusing in an excess of salt solution, the electrical diffusion practically disappears in favour of the " neutral " diffusion. The diffusion coefficient is then in accordance with the frictional-resistance to the driving force of the concentration gradient. In light of previous results this value should be the most suitable for calculating particle size.

## Summary.

1. Using the porous plate method diffusion measurements were carried out on solutions of Orange II, Azogrenadin S, Benzopurpurin 4B, Congo Red, and Chicago Blue 6B in pure water and in excess NaCl.

2. The effects of the electric forces were considered in the discussion of the results. Orange II and Azogrenadin S were found, so far as the experiments went, to be completely or almost completely dispersed into single molecules. Benzopurpurin 4B, Congo Red, and Chicago Blue 6B are aggregated to ionic micelles. This aggregation increases on raising the salt concentration.

3. The mechanism of the salt effect on the aggregation and on the dyeing process is discussed.

4. Experimental evidence presented shows that the frictional resistance of large colloidal ions against osmotic forces is smaller than against electrical forces.

For his assistance in carrying out the experiments I wish to thank Mr. L. Wengert.

I am indebted to the Directors of the I.G. Farbenindustrie Aktiengesellschaft Ludwigshafen a. Rh. for permission to publish this paper.

*Ludwigshafen a. Rh.*
*Hauptlaboratorium der*
*I.G. Farbenindustrie Aktiengesellschaft.*

REFERENCES.

[1] Herzog and Polotzky, *Z. physik. Chem.*, **87A**, 449, 1914.
[2] Freundlich, *Kapillarchemie*, II. Aufl., 1922 ; IV. Aufl., Leipzig, 1930.
[3] Svedberg, *Kolloid-Z.*, **36**, Erg. Bd. 53, 1925.
[4] Pauli and Valkó, *Elektrochemie der Kolloide*, Wien, 1929.
[5] Bruins, *Kolloid-Z.*, **54**, 272, 1931 ; **57**, 152, 1931 ; **59**, 263, 1932.
[6a] McBain and Liu, *J. Am. Chem. Soc.*, **53**, 59, 1931.
[6b] M. E. Laing McBain, *J. Am. Chem. Soc.*, **55**, 545, 1933.
[6c] McBain and Dawson, *J. Am. Chem. Soc.*, **56**, 52, 1934.
[6d] McBain, Dawson and Barker, *J. Am. Chem. Soc.*, **56**, 1021, 1934.
[7] Hartley and Robinson, *Proc. Roy. Soc.*, **134A**, 20, 1931.
[8] Northrop and Anson, *J. gen. Physiol.*, **12**, 543, 1929.
[9] Barnes, *Physics*, **5**, 4, 1933.
[10] Williams and Cady, *Chem. Reviews*, **14**, 171, 1934.
[11a] Fürth, *Kolloid-Z*, **41**, 300, 1927.
[11b] Fürth and Ullman, *Kolloid-Z.*, **41**, 304, 1927.
[12] Nistler, *Kolloid-Beih.*, **31**, 1, 1930.
[13] Dischreit, *Dissertation, Technische Hochschule, Dresden*, 1930.
[14] Schramek and Götte, *Kolloid-Beih*, **34**, 218, 1931.
[15] Bayliss, *Proc. Roy. Soc.*, **81B**, 269, 1909.
[16] Biltz and v. Vegesack, *Z. physik. Chem.*, **73A**, 481, 1910 ; Biltz and Pfenning, *Z. physik. Chem.*, **77A**, 90, 1911 ; Biltz, *Z. physik. Chem.*, **83A**, 629, 1913.
[17] Donnan and Harris, *J. Chem. Soc.*, **99**, 1554, 1911.
[18] Zsigmondy, *Z. physik. Chem.*, **111A**, 211, 1924.
[19] Robinson and Mills, *Proc. Roy. Soc.*, **131A**, 576, 596, 1931.
[20] Schmid, *Z. Elektrochem*, **39**, 384, 453, 1933.
[21] Robinson and Moilliet, *Proc. Roy. Soc.*, **143A**, 630, 1934.
[22] Neale and Stringfellow, *Trans. Faraday Soc.*, **29**, 1167, 1933 ; Garvie, Griffiths and Neale, *Trans. Faraday Soc.*, **30**, 271, 1934 ; Griffiths and Neale, *Trans. Faraday Soc.*, **30**, 395, 1934 ; Hanson and Neale, *Trans. Faraday Soc.*, **30**, 386, 1934.
[23] Haskell (Noyes), *Physic. Rev.*, **27**, 145, 1908.
[24] Arrhenius, *Z. physik. Chem.*, **10A**, 51, 1892.
[25] Hartley, *Phil. Mag.*, **12**, 473, 1931.
[26] Sitte, *Z. Physik.*, **79**, 320, 1932.
[27] Onsager and Fuoss, *J. physic. Chem.*, **36**, 2689, 1932.
[28] Pauli and Valkó, *Kolloid-Z.*, **66**, 312, 1934.
[29] McBain, *J. Am. Chem. Soc.*, **50**, 1636, 1928.
[30] Lorenz, *Raumerfüllung und Ionenbeweglichkeit*, Leipzig, 1922.
[31] Herzog and Kudar, *Z. physik. Chem.*, **167A**, 343, 1934.
[32] Gans, *Ann. Physik.*, (4), **86**, 628, 1928.
[33] Ostwald and Quast, *Kolloid-Z*, **51**, 273, 1930.
[34] Brass and Eisner, *Kolloid-Beih*, **37**, 56, 1932.
[35] Pauli and Weiss, *Biochem Z.*, **203**, 104, 1928.
[36] Haller, *Kolloid-Z.*, **29**, 95, 1921 ; Haller and Russina, *Kolloid-Z.*, **30**, 249, 1922.
[37] Boulton, Delph, Fothergill and Morton, *J. Text. Ind.*, **24**, 113, 1933.

[38] Hill, *Proc. Roy. Soc.*, **104B**, 39, 1928.
[39] March and Weawer, *Physic. Rev.*, **31**, 1072, 1928; *cf.* also Andrews and Johnston, *J. Am. Chem. Soc.*, **46**, 640, 1924.
[40] Paneth and Radu, *Ber.*, **57**, 1221, 1924.
[41] K. H. Meyer, *Melliands Textilber*, **9**, 573, 1928.
[42] Adam, *The Chemistry of Surfaces*, Oxford, 1930.
[43] Hughes and Rideal, *Proc. Roy. Soc.*, **137A**, 62, 1932.
[44] Gorter and Grendel, *Biochem. Z.*, **201**, 391, 1928.
[45] Katz and Samwel, *Ann.*, **472**, 241, 296, 1929.
[46] Volmer, *Trans. Faraday Soc.*, **28**, 359, 1932 ; see also McBain, *The Sorption of Gases by Solids*, London, 1932.
[47] Lennard-Jones, *Trans. Faraday Soc.*, **28**, 333, 1932.
[48] Langmuir, *Physic. Rev.*, **44**, 423, 1933.
[49] Pauli and Valkó, *Z. physik. Chem.*, **121A**, 161, 1926.
[50] Pauli-Valkó, *Kolloidchemie der Eisweisskörper*, Dresden and Leipzig, 1933.
[51] Frisch, Pauli and Valkó, *Biochem.-Z.*, **164**, 412, 1925.

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# THE NATURE OF THE AQUEOUS SOLUTIONS OF DYES.

By Conmar Robinson.

Until the last few years, with few exceptions, most of the work on dyes has been on solutions containing foreign electrolytes. Many of these solutions contain particles large enough to be seen in the ultra-microscope, and are therefore described as colloidal. Others, however, show no ultramicrons, and if they pass readily through membranes and have high diffusion coefficients, it has been customary to say that they are not in colloidal solution.

In the present paper we will describe investigations which we have carried out on highly purified dyes. The properties of the solutions of these pure dyes are very different from those of the solutions which contain even small quantities of electrolytes. Judged by the criterion mentioned above, they would be considered in true solution. On closer study, however, we find that they contain micelles whose size and composition vary considerably in different dyes. The determination of the size and composition of these *submicronic* micelles is one which presents considerable difficulties, and is a problem of general interest to all workers in the field of colloidal electrolytes. The picture we will present of these dyes in solution is, of course, not a final one, as a great amount of further work remains to be done. We believe, however, that it is not likely to be radically modified, and that a point has been reached where we may with advantage discuss the results so far obtained.

The dyes chosen for these investigations are all salts of strong acids or strong bases ; hydrolysis is very small, and therefore does not present a complicating factor as it does in the case of the soaps.

The dyes discussed are :—

## Benzopurpurine 4B.
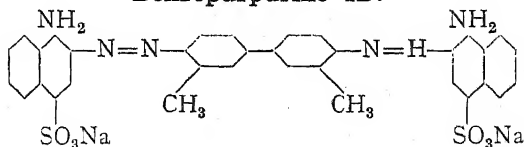
and its isomer prepared from *meta*-tolidine. These two dyes are of considerable interest, as, although they differ only by the position of two $CH_3$ groups, their solutions show some marked differences. Although benzopurpurine 4B is a well-known substantive cotton dye, the *meta*-benzopurpurine does not dye cotton sufficiently to be of commercial importance.

### Bordeaux Extra.
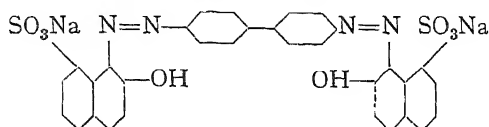


A dye which is more nearly in true solution than the other dyes here mentioned.

### Congo Red.
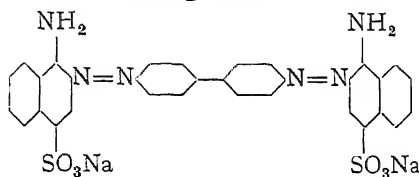


### Congo Rubin.
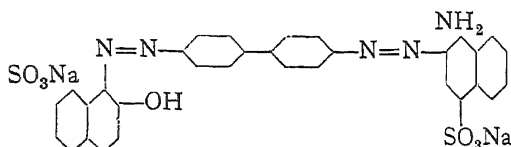


### Methylene Blue.
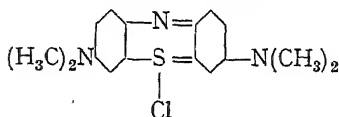


### Purification.

Details of the purification may be found in the previous papers.[1, 2, 3]. The dyes (other than methylene blue) were repeatedly salted out with sodium acetate, and the sodium acetate removed by repeatedly boiling with alcohol. Where found necessary, this was supplemented with crystallisations from water and alcohol-water mixtures. [The criticism of Professor Ostwald [4] of this method of preparation is answered in a paper shortly to appear elsewhere.[3] It may here be mentioned that recrystallisation from water alone after the sodium acetate and alcohol treatment to which he objects, does not produce a dye in a different state.]

The marked effect of removing all traces of foreign electrolytes is most clearly seen in the case of benzopurpurine 4B. As is well known, the solutions of this dye, when containing electrolytes, show needle-shaped

[1] Robinson and Mills, *Proc. Roy. Soc.*, **131A,** 576, 596, 1931.
[2] Robinson and Moilliet, *Proc. Roy. Soc.*, **143,** 630, 1934.
[3] C. Robinson, *communicated to Proc. Roy. Soc.*
[4] Ostwald, *Kolloid Z.*, **68,** 42, 1934.

particles in the ultramicroscope, and become double refracting on streaming. The viscosity may be comparatively high, and depends on the age and method of preparing the solutions. Further, the apparent viscosity is found to vary with the rate of shear.

On the other hand, the solutions of the pure dye are optically empty, show no streaming double refraction and have a low relative viscosity ($1\cdot035$ for a $\frac{1}{2}$ per cent. solution), which is independent of the history of the solution, and does not vary with the rate of shear. All the properties which have been measured, provided $CO_2$ is excluded and the solution does not contain an excess of the acid dye, are found to be reproducible within the experimental error of the measurement, and are independent of the history of the solution. (These remarks also apply to all the other pure dyes we have studied.)

These solutions with reproducible properties and containing no particles large enough to be seen in the ultramicroscope, were the subject of the investigations here described.

## Osmotic Pressure.

The work of Donnan and Harris,[5] Zsigmondy[6] and others has established beyond doubt that dyes such as Congo Red have a high conductivity but a comparatively low osmotic pressure—an anomaly which is found in many colloidal electrolytes. It is most easily explained by assuming some form of aggregate formation amongst the ions. The determination of the degree and type of this aggregation, however, presents difficulties. Thus, in dyes such as Congo Red and Benzopurpurine of the type $Na_2R$, if the aggregates consist of a number of anions, most of the osmotic pressure will be contributed by the sodium ions, and so no direct measurement of the particle size is obtained from the osmotic pressure. It follows, however, as a consequence of Donnan's theory of membrane equilibrium that if the osmotic pressure is measured in the presence of sufficient excess of an electrolyte such as sodium chloride, that when equilibrium has been established the pressure actually measured will be that due to the non-diffusible ions (or particles) only. Consequently, in this way we may obtain a measure of the particle size. Some dyes, Benzopurpurine 4B, for example, are so easily flocculated by electrolytes that it is not possible to add a sufficient quantity without altering the particle size. " Meta " benzopurpurine, however, is only flocculated by large quantities of sodium chloride, and such measurements could be made. This suggested that a $\frac{1}{2}$ per cent. ($N/70$) solution of the dye contained aggregates of at least ten single anions.

Similar experiments by Meier[7] (in Zsigmondy's Laboratory) on Bordeaux extra showed that it was very nearly in true solution.

[The osmotic pressure of these dyes against pure water was

| | |
|---|---|
| *Meta*-benzopurpurine . . . . . . | $1\cdot33$ |
| Benzopurpurine 4B . . . . . . | $1\cdot29$ |
| Congo Red . . . . . . . | $1\cdot20$ |
| Bordeaux Extra . . . . . . | $1\cdot80$ |

where unity is the osmotic pressure which would be expected if the dye existed in solution as undissociated molecules and could be treated as a dilute ideal solution.]

[5] Donnan and Harris, *J. Chem. Soc.*, **99**, 1545, 1911.
[6] Zsigmondy, *Z. physik. Chem.*, **111**, 211, 1924.
[7] Meier, *Dissertation, Göttingen*, 1925.

## Diffusion.

Many attempts have been made to obtain a measure of the particle size of dyes from the diffusion coefficient on the assumption that the Stokes-Einstein equation may be used for this purpose. As Hartley and Robinson [8] have pointed out elsewhere, since dyes are colloidal electrolytes containing multivalent ions, it follows that the diffusion coefficient is given by Haskell's extension of the Nernst equation for electrolytes

$$D = \frac{RT}{F^2} 10^{-7} \left( \frac{1}{z_+} + \frac{1}{z_-} \right) \frac{uv}{u+v} \qquad . \qquad . \qquad . \quad (1)$$

where $z_+$ is the valency of the cation and $z_-$ the valency of the anion and $u$ and $v$ the ion conductivities of the cations and anions respectively. Consequently, since $\frac{1}{z_+} + \frac{1}{z_-}$ can only vary between 1 and 2, $D$ is very largely determined by the mobilities of the ions. Therefore, if the conductivity is high (which is the case in most if not all dyes), the diffusion coefficient must also be high. We cannot obtain even a qualitative value of the particle size from the diffusion coefficient (in electrolyte free solutions) and the attempts to do so have been entirely misleading. It is possible to calculate from the conductivity a minimum theoretical value for the diffusion coefficient. This minimum value was found to be higher than the experimental values previously reported in the literature. The explanation of these low experimental figures is that the electrolytes have not been completely removed. If a solution of the pure dye is allowed to diffuse into water, the rapidly diffusing non-colloidal ions (*e.g.* sodium ions) will tend to diffuse away from the slowly diffusing colloidal ions or particles. In consequence, a potential gradient is set up in the solution, and the non-colloidal ions tend to pull the colloidal ions along with them. This accounts for the high diffusion coefficient predicted by equation (1). If, on the other hand, a large quantity of an electrolyte such as sodium chloride is added to the dye solution, and the water into which it is diffusing, then in this highly conducting medium no potential gradient will be set up and the colloidal ions will diffuse independently of the " gegenionen " and in accordance with the Stokes-Einstein equation. Consequently, a much lower diffusion coefficient is obtained. With smaller quantities of added electrolytes we will find intermediate values. This will be seen from Fig. 1, where diffusion coefficients of *meta*-benzopurpurine and Bordeaux extra are shown, both for the pure solutions and for increasing quantities of sodium chloride. It will be seen that there is first a very rapid fall in the diffusion coefficient, but that the slope of the curve gradually becomes less, and eventually the diffusion coefficient becomes constant over a considerable range of sodium chloride concentration (with Bordeaux extra the concentration of sodium chloride could not be carried so far as with *meta*-benzopurpurine, on account of the former dye being more easily flocculated). Where the curve is horizontal, we may conclude that the limiting condition has been reached where the colloidal ions diffuse independently of the *gegenionen*, and where the Stokes-Einstein law is applicable (assuming, of course, that the particles are spherical). On the other hand, we may also assume that the concentration of electrolytes has not been great enough to increase the degree of aggregation

[8] Hartley and Robinson, *Proc. Roy. Soc.*, 134A, 20, 1931.

of the dye. In Table I. are given the values of the particle weight calcu-
lated, assuming a density of 1·5 (which was found to be the density of the
solid dye). Since the molecular weights of both dyes are about 700, it
will be seen that the Bordeaux extra only shows a small degree of anion
aggregation. With *meta*-benzopurpurine, however, we obtain a figure of
17 for the number of anions in the particle. This value is open to doubt,
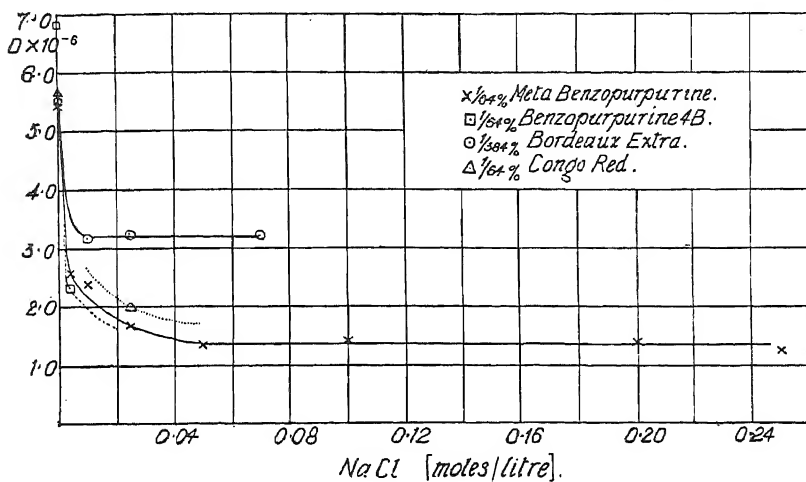


FIG. 1.

as the exact value which should be taken for the density of the particle
is not known, but as in the case of the osmotic pressures in the presence
of salt, where the limiting osmotic pressure was approached but not
actually reached, it points to a value of over ten. The percentage of
included sodium in the anion aggregate (which we will discuss later)
would of course not greatly affect these results.

TABLE I.

| Dye. | $D \times 10^{-6}$. | | Particle Weight. | Molecular Weight. |
|---|---|---|---|---|
| | In Water. | Limiting Value in NaCl. | | |
| *Meta*-benzopurpurine . | 5·43 | 1·35 | 12,300 | 726 |
| Bordeaux extra . | 5·55 | 3·25 | 900 | 700 |
| Benzopurpurine 4B . | 6·82 | [1·20] | 18,000 | 726 |
| Congo Red . . | 5·67 | [1·70] | 6,000 | 698 |
| Congo Rubine . . | 5·59 | — | — | 699 |

The figures in brackets are obtained by extrapolation and are not reliable.

As with the osmotic pressure method in the presence of electro-
lytes, this method of determining the particle size is not applicable to
those dyes, such as Benzopurpurine 4B, which are flocculated by low
concentrations of electrolytes. A value for the diffusion coefficient at
a lower concentration of sodium chloride is, however, given. If the
curve is assumed to run parallel to that for *meta*-benzopurpurine, it would

seem that the particle size is somewhat greater than that of *meta*-benzo-purpurine.

## The Mobilities.

Further information about the particle size and its dependence on concentration, as well as some indication of the amount of sodium included in the anion complex may be obtained by accurate determination of the radical mobilities. The mobility is obtained from the conductivity and transport number measurements, the latter being discussed in more detail in another paper to be read at this meeting. This information is therefore obtained from the pure solutions without the necessity of adding other electrolytes, and is therefore applicable to dyes such as Benzopur-purine 4B.

Moilliet [2] has carried out such measurements on Benzopurpurine 4B, *meta* - benzopurpurine and Bordeaux extra, and his results are shown in Fig. 2. Assuming the mobility to be proportional to $z/r$ where $z$ is the charge and $r$ the radius of the particle and that consequently the mobility increases with increasing aggregation, we may draw the following conclusions. Bordeaux extra exists in very dilute solutions in the form of single ions, or nearly so, but is to some extent aggregated in more concentrated solutions as is shown in the curve by the increase in the mobility with increasing concentration. *Meta*-benzopurpurine is more highly aggregated than Bordeaux extra at all the concentrations measured; here also, with lower concentrations, we find an increase of mobility with increasing concentration, showing aggregation increasing with increasing concentration. The subsequent decrease of the mobility with increasing concentration, after reaching a maximum, is due to the effect of the interionic forces and increased inclusion of sodium overcoming the initial effect of aggregation. Benzopurpurine 4B, with the highest mobility is the most highly aggregated; here the maximum in the mobility curve was evidently at a concentration below the lowest used in the experiments, and we have not reached that part of the curve where mobility increases with increasing concentration.

FIG. 2.

- ▣ Benzopurpurine 4B.
- ⊙ *Meta*-benzopurpurine.
- △ Bordeaux Extra.

If we assume only one type of micelle present, the fraction of free sodium present in the solution will be given by [2]

$$f = \frac{\lambda}{l_{Na} + v_R}$$

where $l_{Na}$ is the equivalent conductivity of the free sodium ions. The value of $f$ will be in doubt, owing to the uncertainty about the value of $l_{Na}$. If this is taken as equal to the value of $l_{Na}$ in NaCl, we shall obtain a minimum figure for $f$, *i.e.*, a maximum figure for the included sodium. In this way we find that the included sodium is not more than 25 per cent. in the 0·5 per cent. benzopurpurine solutions, and very much less in the case of Bordeaux extra.

The mobility of *meta*-benzopurpurine at no point on the curve exceeds that of Bordeaux extra by more than 50 per cent. On the other hand, we concluded that the *meta*-benzopurpurine particle contains more than 10 anions, while that of Bordeaux extra contains less than two. This would mean that neglecting the interionic forces, the $v_R$ of the *meta*-benzopurpurine would be at least three times the $v_R$ of Bordeaux extra.

The interionic forces, which of course will reduce the mobility of the high valency *meta*-benzopurpurine particles much more than that of the low valency Bordeaux extra particles, will reduce this discrepancy, but it seems improbable that the effect of these forces could be great enough to account for all the difference. Another factor which has been neglected is the asymmetry of the particle. If this was considerable, it would mean that the value of the particle size obtained from the diffusion measurements would be higher than the real value; on the other hand, we would expect a greater difference between the results obtained from the osmotic pressure and diffusion measurements respectively.

There is therefore a quantitative disagreement between the diffusion and osmotic pressure measurements on the one hand and the mobility results on the other. To what extent this difference is accounted for by asymmetry and the interionic forces can only be cleared up by further investigation.

The solutions of the two benzopurpurines, as has been mentioned, show certain striking differences. Thus, Benzopurpurine 4B in the presence of sufficient electrolytes shows needle-shaped ultramicrons, streaming double refraction, structural viscosity, ageing, etc. On the other hand, it has never been found possible to prepare a solution of *meta*-benzopurpurine containing ultramicrons or showing streaming double refraction. Benzopurpurine 4B has a fairly sharp flocculation value with, for example, sodium chloride, at which concentration the whole dye flocculates, leaving a colourless supernatant liquid. *Meta*-benzopurpurine, however, is not only much less sensitive to salts, and although the dye is partly precipitated by NaCl at concentrations of from 2·2 to 2·7 normal, there is no sharp flocculation value, the effect of the salt apparently being more like a reduction of solubility than the flocculation of a colloid. These differences together with the fact that Benzopurpurine 4B is held up by coarser ultrafilters than is *meta*-benzopurpurine, led us in an earlier paper to conclude that Benzopurpurine 4B contained much larger particles than the *meta*-dye. But, considering all the evidence, it seems unlikely that the difference in the particle size, at least in the higher concentrations, is very great (the ultrafiltration experiments where such small particles are concerned must be looked upon as very difficult to interpret). It seems possible that the

marked difference in behaviour to electrolytes may be connected with the fact that, as the mobility experiments show, Benzopurpurine 4B breaks up less readily on dilution than does the *meta*-dye, so that in quite dilute solutions Benzopurpurine 4B is still far from being ionically dispersed.   This must have its origin in a difference in the arrangement of the ions constituting the micelle, so it may be that the difference in the properties of the salt-containing solutions has its origin not so much in a difference in particle size as in a difference in the construction of the particles, *i.e.*, the ions in the particles being differently oriented with respect to one another.   Although none of the experiments here described gives any direct evidence of this possibility, indirect evidence has recently been obtained by Professor Freundlich,[9] who has shown that the pure solid Benzopurpurine 4B (when pasted with its saturated solution) shows plasticity and no Osborne-Reynolds phenomenon, while *meta*-benzopurpurine shows no plasticity but distinct Osborne-Reynolds phenomenon— suggesting long-shaped particles in the pure Benzopurpurine 4B and spherical in the *meta*-benzopurpurine.   A tendency of the molecules to build up differently constructed micelles might be expected to be accompanied by different powers of dyeing cotton, as are actually found.



FIG. 3.

× A highly purified specimen.
⊙ A second specimen probably less pure.

## The Conductivity of Methylene Blue.

The particle weights of these dyes are all under 20,000, and as a consequence of this low particle weight, some of them (*e.g.*, *meta*-benzopurpurine) might have been mistaken for ionically dispersed solutions which do not contain micelles, if a systematic study of their properties had not been carried out.   The interesting question consequently arises : do those dyes such as methylene blue, which in the past

[9] Freundlich, *J. Soc. Chem. Ind.*, **53**, 222T, 1934.

have been considered in " true solution," exist in solution as separate ions, or do they form micelles ?

A complete examination of any such dye by methods similar to that used for *meta*-benzopurpurine is a lengthy research. It is therefore desirable to introduce some method which will give some information about micelle formation in a comparatively short time. Methylene blue is a case where such information may be obtained from the shape of the conductivity-concentration curve at low concentrations, as has been shown by recent measurements carried out by H. E. Garrett and the author. A specially purified sample of this dye was obtained from British Drug Houses, Ltd., and further purified by recrystallisation from alcohol and from water. In Fig. 3 the equivalent conductivity is plotted against the square root of the concentration. If the dye behaved as an ordinary univalent electrolyte, we would expect this to give a straight line, $\lambda$ decreasing continually with increasing concentration. The curve actually obtained has a very pronounced maximum in it, and $\lambda$ reaches a value of 109. The increase in the conductivity before this maximum is reached can only be explained by the formation of micelles having a higher conductivity than the single cations, this micelle formation increasing with increasing concentration. [It seems possible that conductivity measurements of Benzopurpurine 4B at very low concentrations might reveal a similar maximum in these dyes. We are now investigating this point. When the measurement described by Robinson and Moilliet [2] were carried out, the very good conductivity water ($\kappa = 0.3 \times 10^{-6}$) used for the methylene blue measurements was unfortunately not available.]

## Summary.

We have then this picture of the solutions of the dyes studied. They contain micelles consisting of a number of anions with some included sodium. The constitution of these micelles may be expressed as that of an apparent mean micelle, the existence of this apparent mean micelle being the simplest assumption. If other micellar types exist, the different types must be in rapid equilibrium with one another, as is shown by the sharpness of the boundary in the transport number experiments.[2] The structure of this micelle is probably quite definite, that is to say, the ions have a definite orientation as in a micro crystal. The micelle of *meta*-benzopurpurine from diffusion and osmotic pressure measurements appears to contain at least ten particles with not more than 25 per cent. included sodium. The micelles of Benzopurpurine 4B are somewhat larger, but of the same order, the included sodium being about the same. The ions in the micelle of the latter dye are probably differently arranged, the resultant micelle being more long shaped. The break-down of the micelle with progressive dilution is greater in the case of the *meta*-benzopurpurine.

Bordeaux extra is a dye much more nearly in true solution. Even here, however, in the 0.5 per cent. solution there is appreciable association, this getting less with progressive dilution.

Congo Red, which has not been so completely studied as the above-mentioned dyes, it would seem has particles somewhat smaller than *meta*-benzopurpurine.

Methylene Blue, a dye which was believed to be in true solution, associates into micelles sufficiently to make this evident in the conductivity curve.

*The Sir William Ramsay Laboratories of*
  *Inorganic and Physical Chemistry,*
    *University College, London, W.C.1., and*
      *Imperial Chemical Industries, Ltd.*

## GENERAL DISCUSSION.[*]

**Dr. E. Valkó** (*Ludwigshafen a/Rh*) (in introducing his paper) said : The method applied is excellently suitable for investigating the rôle played by particle size in the technique of dyeing. For instance, the mode of action of level dyeing agents and their relationship to the particle size has been repeatedly discussed, but the question has not been dealt with experimentally. We have now investigated the influence of Peregal O, a new level dyeing agent, an organic, non-electrolytic, large molecular substance, especially effective in vat dyeing.[1, 2] As object we used a dyestuff of the indanthrene series; namely, Indanthrenbrillantgrün (identical with the famous Caledon Jade Green) in the form of its leuco-salt. We found the aggregation number of the dye about 3. In the presence of Peregal O the apparent aggregation number was about 420. In contradiction to earlier assumptions, the association degree of dye is very slight, particularly taking into account the large salt concentration (0·2 $N$ NaCl) and the low temperature (25°). The forced aggregation, which was produced by the addition of the level dyeing agent is surprising. We must conclude that to each particle of level dyeing agent are attached many dye molecules. We have here to do with a case where, in opposition to the salt effect, increasing aggregation leads to reduction of affinity. The orthodox particle size theory, is unable to explain this fact. If, however, we go back to the molecular mechanism, the phenomenon will be comprehensible. The salt effect on dyeing is a sort of salting out, but the essence of the case dealt with lies in the competition for the dye between the level dyeing agent and the fibre.

We have also investigated the effect of the level dyeing agent on a direct cotton dye, Chicago Blue 6B. The results indicate that the level dyeing agent does not protect the dye against the influence of salt, but even increases this influence, by making the dye more aggregated.

We have recently begun an investigation into the diffusion coefficient of dyes at the temperature of 90°. As a preliminary result we obtained for Benzopurpurin 4B (weight conc. = 0·01 per cent. ; NaCl–solution = 0·01$N$) an aggregation number of about 2.

(*Communicated*) : According to a private communication from Professor Ostwald the experimental conditions, observed by him and Quast correspond more to the assumption used as the basis of the calculation in their first paper.[3] The values obtained here and not those later communicated [4] and quoted in my paper are to be regarded as correct.

These values are :

Congo red :         $D = 0·21 — 0·27$ cm.²/day
Benzopurpurin 4B : $D = 0·16 — 0·22$    ,,

both for a concentration of 0·02 — 0·01 per cent.

**Professor E. Elöd** (*Karlsruhe*) said : In reference to Dr. Valkó's interesting statements on the influence of the particle size on the substantive dyeing of chromium leather, I may make the following remarks.

* On three preceding papers.
[1] Schwen, *Melliands Textilber*, **14**, 22, 1933.
[2] Schöller, *ibid.*, **15**, 357, 1934.
[3] Ostwald and Quast, *Kolloid-Z.*, **48**, 83, 1929.          [4] *Ibid.*, **51**, 273, 1930.

The degree of dispersion of the substantive dyestuffs has an influence generally only in those $p_H$ regions in which, so to say, only the *physical* partial process of dyeing, *i.e.* the diffusion into the interior of the leather fibres plays a part. In this $p_H$ region which lies on the alkaline side of the isoelectric point, commercial dyeing is carried out only in exceptional cases for the purpose of attaining specific results. In ordinary cases of dyeing, *i.e.* on the acidic side of the isoelectric point, and even in the marked acidic cases of the general technical chromium leather, *i.e.* at about $p_H = 4$, the decisive rôle is played by the *chemical* partial processes of dyeing. Accordingly, the sulpho-acids of the substantive dyestuffs will react chemically with the basic groups of the leather in their superficial layers and will be bound there in ordinary dyeing. The quantities of dyestuff employed and bound by leather proteins are generally far below chemical saturation. Thus the dyestuffs will be retained only in the superficial layers, sufficient dyestuff, as a rule, not being available—after saturation of these layers—for the inner layers. Only those dyestuffs which show insufficient fastness against water (*i.e.* which can easily be separated by dissociation from the combination of protein-dyestuff, *viz.* dyestuff acid), will again on their part follow the laws of dispersion. (See E. Elöd and H. Hänsel, *Collegium*, 766, 1933.)

**Dr. Conmar Robinson** (*London*) said : I would be very interested to hear if Dr. Valkó has found any evidence of this dependence of the apparent diffusion coefficient on the pore size of the disc. As Dr. Valkó has stated in his paper, McBain has shown that an apparatus similar to that used by Dr. Valkó (*i.e.* involving sintered glass discs) gives reliable results for the diffusion coefficients of soaps. It does not follow, however, that there will not be serious errors due to surface effects when using dyes. The diffusion measurements that I have carried out on dyes have been done with a micro-diffusion apparatus as used by Nistler. Before constructing this apparatus we did consider using the sintered glass disc method, which, under favourable conditions, we would expect to give a much higher degree of accuracy. Mr. Hartley was good enough to carry out some preliminary experiments on dyes in an apparatus using Jena sintered glass discs. With electrolyte free " meta " benzopurpurine it was found that the apparent diffusion coefficient using a G. 3 disc was 20 per cent. higher than that using a G. 4 disc. These results were repeated several times and were found to be reproducible. With KCl the results obtained with the two discs differed by less than 1 per cent. Dr. Valkó has not carried out experiments with " meta " benzopurpurine, but I think he will agree that one would expect the error due to surface effects to be, if anything, less than that with benzopurpurine 4B.

**Professor H. Freundlich** (*London*) said : I should like to ask Mr. Valkó : In colloidal work it is frequently necessary to compare a strongly colloidal dyestuff with a dyestuff whose solution is, as far as possible, a true solution. For the latter purpose methylene blue was often used, but the experiments of Mr. Robinson show that even not very concentrated solutions of this dyestuff contain undoubtedly a marked number of micelles. May I draw the conclusion from Table IV. of Mr. Valkó's paper that Orange II and azogrenadin S are really suitable examples of dyestuffs giving true solutions ? Then there is a point in Mr. Robinson's paper which I would like to know more about. He remarks : " There is therefore a quantitative disagreement between

the diffusion and osmotic pressure measurements on the one hand and the mobility results on the other." It would be valuable to know what is the order of magnitude of this disagreement. In the discussion of Mr. Robinson's experiments I did not find an answer to this question.

**Dr. E. Valkó** (*Ludwigshafen a/Rh*) said : Professor Freundlich's question may be answered by pointing out that, according to Table IV. of my paper, Azogrenadin S and Orange II in a concentration below about $1/1000$ $N$ are, at least as to 80-90 per cent., dispersed in single ions. The diluted solutions of these dyes must therefore be regarded as true solutions.

In answer to the question of Dr. Robinson, I should like to remark that I have not observed any dependence of the diffusion velocity on the pore size of the porous disc. For most experiments I have used G. 4 plate. However a small number of measurements have also been carried out with G. 3 membrane. The deviations were then no larger than in the other cases (3-5 per cent.). A dangerous source of error can be produced by insufficient purification of the plates. The cleaning acid must be carefully washed out, preferably with diluted ammonia and the purity controlled by measurement of conductivity.

**Dr. Conmar Robinson** (*London*) said : Professor Freundlich asks whether Orange II. and Azogrenadin S are "really suitable examples of dyestuffs giving true solutions." I think the evidence from Dr. Valko's work is quite definite that these dyes show some small degree of aggregation as does the dye Bordeaux Extra which I have discussed in my paper. Such a dye might be used as a substitute for a dye in "true solution" provided this degree of aggregation was not great enough to be of importance in the problem being studied. But whether or not this degree of aggregation could be considered as negligible would depend entirely on the nature of the particular problem.

Professor Freundlich's other question may be answered as follows : Both mobility and diffusion experiments point to Bordeaux Extra being very nearly dispersed as single ions. Diffusion measurements indicate that the micelle of "*meta*" benzopurpurine contains about eleven anions, and the osmotic pressure results are approximately in agreement with this. The mobility of the micelle, neglecting interionic forces and assuming the particle to be spherical, would be proportional to $z/r$ where $z$ is the charge and $r$ is the radius. The ratio of the mobilities of these two dyes will then, according to the information obtained from the diffusion measurements, be *at least* $3 : 1$, unless we assume impossible values for the included sodium. The ratio of the mobilities actually found was about $1\cdot5 : 1$. It seems unlikely that the factors neglected, interionic forces and asymmetry, can account for all the discrepancy. There is, however, another possible explanation. Both osmotic pressure and diffusion experiments are conducted in the presence of electrolytes. It has been assumed (for these two dyes) that since constant diffusion coefficients were obtained over a considerable range of salt concentration that the salt had not changed the degree of aggregation. It is, however, possible that a change of aggregation took place at a *low* concentration of salt (where the diffusion coefficient is still falling, see Fig. 1) and that after this further addition of salt did not affect the aggregation. An investigation we are about to carry out may decide this matter.

**Professor E. Elöd** (*Karlsruhe*) said : In reference to the interesting statements of Dr. Robinson, I may point out that in dyeing wool or

natural silk with substantive dyestuffs (as, for instance, diamine-sky-blue FF) the velocity of the taking up of the dyestuff can be markedly influenced. In one case we used a commercial preparation, in the other a dialysed preparation (*not electro*dialysed !), to which we added as much salt as was present from the beginning in the commercial product. We saw that the commercial product, *i.e.* the product made, dried and stored in the presence of electrolytes showed a greater diffusion velocity in the fibres than the dialytically purified product. The proportions can be seen from Fig. 3 in Elöd's paper.[5]

**Mr. G. S. Hartley** (*London*), in reply to Dr. Valkó's question on the diffusion measurements by the porous plate method referred to by Dr. Robinson, said that he did not think residual acid in the freshly-cleaned discs used could explain the discrepancy referred to because, in the case of the diffusion in excess of salt, where the discrepancy was still found, the discs had been washed with alkali after the acid treatment and before use.

In reply to Mrs. McBain he said that the discs used had behaved normally with potassium chloride solutions after the dye diffusion measurements had been made and when they had been washed only with water in between. In view of the results of Dr. Valkó, however, the speaker said that his own measurements, which were admittedly few in number, should be repeated.

The speaker expressed doubt as to the validity of the distinction made in the concluding section of Dr. Valkó's paper between electrical and neutral diffusion in the case of a pure colloidal electrolyte diffusing in water. This distinction was tantamount to giving the ionic mobilities different values in the " diffusion pressure " and " electrical potential gradient " terms of the equations for the ionic diffusion, the value in the former being the infinite dilution one and in the latter the electrical mobility as ordinarily observed. He had himself considered this possibility in a previous paper but now thought it highly improbable. The essential thing was that the ions of the diffusing pure electrolyte, no matter what the nature of the forces acting on them, must diffuse at equivalent rates, and hence both the relaxation and endosmotic terms of the Onsager mobility equation must disappear in their usual form, the former disappearing altogether while the latter, as Onsager and Fuoss have shown, appears much reduced in magnitude and as a different function of concentration, as a positive term. Every diffusion process is equal and opposite to some sedimentation process since the former can always be arrested by the application of a suitable force on the diffusing solute. This equivalence is very useful since the sedimentation process is so much more simple to picture, and there can be no doubt that in the sedimentation of a pure electrolyte *neither* term of the Onsager mobility equation enters in its usual form. It seemed to the speaker that a more probable explanation of the diffusion coefficient of pure benzopurpurine 4B being considerably lower than the calculated value would be the low value of the $\left( 1 + \dfrac{d \log f}{d \log c} \right)$ term.

The speaker also suggested that the slight diminution of the diffusion coefficient in excess of salt with increasing concentration of salt was not *necessarily* evidence of increasing aggregation, for, in the case of diffusion in excess of salt, although the activity coefficient term

[5] *Cf.* this vol., page 220.

becomes unity and the endosmotic term of the Onsager mobility equation disappears, *the relaxation term in this case re-appears* because the ions constituting the atmosphere of the diffusing particle no longer move with the particle. Since, however, they do not move in the opposite direction but only remain stationary, this term will be smaller than in the conductivity case, and indeed about half the size. A *slight* diminution of diffusion coefficient with increasing concentration of salt is therefore to be expected even if the aggregation remains unchanged. Experimental evidence of this was found by the speaker in unpublished measurements on the diffusion of the permanganate ion in excess of potassium nitrate.

Finally the speaker expressed doubt as to whether the discrepancy between the mobility of the benzopurpurine aggregate calculated from the measured diffusion in excess of salt and the value observed by Robinson and Moilliet in the pure solution could be quantitatively accounted for by " atmosphere " effects. These effects would have to account for a fall from 100 to 54 in a solution of concentration about $0.0007N$. The fall to be expected from application of equation (30) of the speaker's own paper (No. 6) to the figures given by Dr. Valkó would be about 25 per cent., and, as pointed out in that paper, this estimate is likely to be too great. A similar discrepancy is commented on by Robinson in his paper (p. 250). It is worth while to remember that these discrepancies are between measurements made in excess of salt and those made in the pure solution. A possible explanation therefore is that the addition of a small amount of salt considerably increases the degree of aggregation of the dye, which is subsequently not greatly increased by further addition of salt except in the cases where flocculation occurs.

**Dr. E. Valkó** (*Ludwigshafen a/Rh*) (*communicated*), in reply, said : Mr. Hartley doubts the validity of the differentiation made by me between electrical and neutral diffusion for the case of the diffusion of pure colloidal electrolytes in water. I have, however, expressed in my paper the opinion that, in this case, the electrical diffusion of the colloidal ion completely outweighs its neutral diffusion, and consequently the diffusion constant here corresponds with the frictional resistance in the electric field. In other words, the differentiation has no importance so long as this case is considered by itself. If we calculate the diffusion constant for benzopurpurine 4B in 0.02 per cent. solution on the basis of equation (1) of my paper, taking $u = 50$ and $v = 54$ rec. ohms and assuming an aggregation number of 5, we obtain for $D$ the value 0.65 cm.$^2$/day, while the experimental value is $0.624 \pm 0.03$ cm.$^2$/day (Table I.).

I agree with Mr. Hartley that the interionic forces can explain a small fall of diffusion constant with increasing salt concentration without it being necessary to assume any influence on the aggregation. As explained in the paper I intentionally neglected the influence of the interionic forces on the diffusion in calculating the aggregation numbers. I consider it, however, very improbable—and I think Mr. Hartley will agree—that in the observed fall of the diffusion constant to half its initial value, in the case for example of Chicago Blue 6B, these forces will take a quantitatively significant part.

I hold in common with Mr. Hartley the belief that a simple explanation, as an " atmosphere " effect only, of the observed discrepancy between electrical mobility in pure solutions and aggregation numbers

obtained from diffusion in presence of salt, can scarcely be given, and that, by the assumption that the aggregation in dilute salt solution is significantly greater than in pure water the discrepancy can be reduced to the vanishing point. On these grounds, the fact that an analogous discrepancy in other cases, and particularly in egg-albumin, has been described and discussed, seems to me particularly important. In the case quoted the existence of the anomaly has been established with complete certainty, because particle-size, charge and mobility have been obtained by a variety of methods (*e.g.* ultra-centrifuge, osmotic pressure, membrane potential, activity, conductivity, Hittorf transport and moving boundary). I would like to take this opportunity to point out that the proteins, as a consequence of their relatively slight tendency to associate and the possibility of conveniently determining their charge, constitute a much more suitable subject for the application of electrolyte theory, and in particularly of the Debye-Hückel theory, than the dyes with their strongly variable degree of aggregation.

**Mr. G. S. Hartley** (*London*) (*communicated*), in reply, said : In regard to Dr. Valkó's opinion that the proteins form more suitable subjects for the application of electrolyte theory than the aggregating simple electrolytes, I agree that this is true in so far as changing aggregation is a complication, but I do not think that the charge of a protein particle can be more conveniently or more certainly determined. In the case of the aggregating simple electrolytes we derive a value for the " charge " of the particle from its size and the known equivalent weight of the electrolyte which is the exact counterpart of the value obtained for the protein particle by measurement of the number of protons adsorbed. The question of how far the simple oppositely charged ions balancing the charge of the particle are kinetically free in the diffuse atmosphere or temporarily attached to the particle by electrostatic forces is of equal difficulty in both cases. We can, in short, measure the number of protons adsorbed by the particle, but do we know how many simple anions, other than OH ions, are also adsorbed in consequence of the resulting positive charge ? I agree that a large part of the discrepancy between the values of 30 and 6 in the case quoted can be explained by " atmosphere " effects—a larger part than in the dyes because the charge is greater and the particle larger—but it is doubtful whether the whole discrepancy has to be explained in this way.

**Dr. O. Quensel** (*Upsala*) said : I have read the papers of Dr. Valkó and Dr. Robinson with the greatest interest as I have done some researches myself on Congo Red solutions by means of Professor Th. Svedberg's ultracentrifuge.

From measurements of the sedimentation equilibrium one can calcuate the molecular weight of the substance in solution if one know the lconcentration at different distances from the centre of rotation, afte equilibrium is reached. A criterion that the particles in the solution all are of the same size is that the same value for the molecular weight in layers of solutions, at different levels in the cell be found. If, however, the particles are different in size, higher values for the molecular weight are obtained in the outer part of the solution. Now I have determined the molecular weight in some Congo Red solutions by means of this method. The concentration of the Congo Red in those solutions was of the order of 0·01 per cent. and the solutions also contained some other electrolyte, as a rule about 0·1 m. sodium chloride. I have always found that the

calculated value for the molecular weight was independent of the distance from the centre of rotation and in all cases the molecular weight was found to be something between 8000 and 9000. I cannot give the exact value yet, because I have first to determine certain constants more accurately. My results show that the Congo Red solutions, which I have examined by means of equilibrium runs, consist of well-defined particles, all equal in size. That is, the solutions are monodisperse. I therefore quite agree with Dr. Robinson when he suggests that the structure of the micelle in some dyestuff solutions is quite definite, that is to say, the ions have a definite orientation as in a micro crystal.

The ultracentrifuge can also be used in another way. It is possible to measure the sedimentation velocity and calculate the sedimentation constant. The sedimentation constant is a function of the size and the shape of the particles. In all the solutions previously investigated by means of the sedimentation equilibrium method, the Congo Red had a sedimentation constant which was about $1\cdot4 \times 10^{-13}$. But in several other solutions, especially in solutions containing larger concentrations of sodium chloride, other values for the sedimentation constant have been found. But I have not obtained more than three different values for the sedimentation constant, namely $1\cdot4$, $1\cdot75$ and $2\cdot1 \times 10^{-13}$ (mean values). Unfortunately, I cannot give the molecular weight of the Congo Red in those solutions where the sedimentation constant is $1\cdot75$ and $2\cdot1 \times 10^{-13}$ because determinations of the molecular weight by means of equilibrium measurements are still to be made. And one cannot, as a rule, calculate the molecular weight from values of the sedimentation constant. But even if this is impossible, one can calculate a more or less probable value for the ratio of those molecular weights, which correspond to certain values of the sedimentation constant. Then you will find that the values $1\cdot4$, $1\cdot75$ and $2\cdot1\cdot10^{-13}$ correspond to molecular weights, the ratio of which is about $2:3:4$. Therefore I think that it is possible that the sedimentation constants $1\cdot75$ and $2\cdot1\cdot10^{-13}$ correspond to molecular weights which are $1\cdot5$ and $2$ times greater than about 8500, which is a mean value for the molecular weight corresponding to the sedimentation constant $1\cdot4\cdot10^{-13}$. If this is true, I think the three values found for the sedimentation constant may correspond to solutions containing micelles which consist of say 12, 18 and 24 single-dyestuff ions.

I was therefore very interested when Dr. Valkó mentioned that he had found values for the diffusion coefficient of Congo Red, corresponding to micelles containing about 12 and 24 dyestuff ions; in his paper, Dr. Valkó has only calculated the molecular weight from two values of the diffusion coefficient. If all his values are used, one will find three different values of the molecular weight, the ratio of which are also about $2:3:4$. Determinations of the molecular weight by means of equilibrium runs were carried out at 20° C. The centrifuges, used for equilibrium measurements, are running in a thermostat and the temperature can therefore be varied. But even then it would be difficult to make experiments at the very high temperature used in the dyeing process.

The velocity runs are carried out with another type of centrifuge, which is not thermostated. It is therefore impossible to make runs at any given temperature. The actual temperature will depend upon operation conditions. In my velocity runs, the temperature was some degrees above 30° C. The values of the sedimentation constant, obtained at this temperature, were corrected so that they correspond to a temperature of 20° C.

**Dr. J. H. Northrup** (*Rockefeller Inst., Princeton*) (*communicated*) : The porous plate method for the determination of the diffusion coefficient was originally devised by Anson and myself as a means for determining the size of molecules present in mixtures of unknown composition. Under these conditions sedimentation methods cannot be used. It was pointed out that Einstein's equation connecting the diffusion coefficient with the radius applies only to uncharged particles, so that the calculation of the size of an ion was uncertain. At that time the theory of the influence of ionisation and the presence of other ions on the rate of diffusion was not sufficiently established to be of practical use. The work of McBain and collaborators, Onsager and Fuoss, Hartley and Robinson, and Dr. Valkó has made it possible to calculate at least approximately the rate of diffusion of an ionised substance in the presence of various concentrations of electrolyte. It is now possible, therefore, to gain some information as to the degree of ionisation as well as the size of an unknown substance by diffusion measurements carried out in the presence of various concentrations of neutral salts.

**Professor F. G. Donnan** (*London*) said : The remarks of Dr. Quensel are extremely valuable and important, and we shall all look forward with the greatest interest to the publication of his work. The application of the ultracentrifuge method in Professor Svedberg's laboratory to the study of solutions of dyestuffs will be sure to lead to results of the greatest importance.

**Dr. S. M. Neale** (*Manchester*) (*communicated*) said : My own experience confirms Dr. Valkó's statement that the accuracy of the McBain diffusion method is, in the case of dyestuffs, only about 5 per cent. In fact, using an apparatus very similar to Dr. Valkó's we often obtained even larger variations. This was attributed to inadequate stirring of the solutions. In the case of relatively concentrated solutions of highly soluble electrolytes as used by McBain gravitational mixing is much more effective than with the dilute solutions used in working with dyestuffs.

**Dr. G. S. Adair** (*Cambridge*) said : In studies of the effects of salts on the diffusion of dyestuffs, it may be noted that the simplest conditions are obtained when the product of the activities of the diffusible ions such as Na and Cl is the same in the colloidal solution and in the liquid adjacent to it. The recent work of Tiselius and Gross on the free diffusion of hæmoglobin and albumin gives lower values for the coefficient of diffusion than those obtained with the glass membranes, described by Northrop and Anson. The lower values are in accordance with the view that the proteins are hydrated.

# THE DYEING OF CELLULOSE WITH DIRECT DYESTUFFS ; THE IMPORTANCE OF THE COLLOIDAL CONSTITUTION OF THE DYE SOLUTION AND OF THE FINE STRUCTURE OF THE FIBRE.

BY T. H. MORTON.

## I. Introduction.

In spite of the comparatively large volume of literature dealing with the substantive cellulose dyestuffs—direct cotton dyes—and their dyeing properties, there has been until recently a lack of accurate quantitative data dealing with the fundamentals of the dyeing process. Much of the earlier work is vitiated by the employment of ill-defined experimental materials : for example deductions concerning the polydispersion of dye solutions have been drawn from observations of colour changes which must definitely be assigned to the use of a sample of dyestuff containing more than one coloured substance.

The technology of the application of the direct dyes to cellulosic fibres, both natural and artificial, has naturally received considerable attention, but it has not been possible to correlate this mass of information by means of any completely acceptable dyeing theory.

In the last three years, however, a quantitative survey of the direct dyeing process has been taken up in two laboratories,[1, 2] with the result that a considerable clarification of theoretical principles is possible. These researches, using carefully purified and characterised materials and adequate analytical methods, have demonstrated the following points:

(*a*) If the dyeing of a cellulosic fibre or sheet is sufficiently prolonged a true reversible equilibrium partition of dye between solid and solution is attained. At equilibrium the dye in the dyed material is distributed uniformly throughout its bulk.

(*b*) The kinetics of the dyeing of regenerated cellulose with direct dyes are approximately those to be expected of a process controlled by the diffusion of a solute from the bath into the material being dyed.

(*c*) Viscose yarns of differing " dyeing affinity " differ mainly in the speed of attaining equilibrium, and not in the equilibrium finally attained.

(*d*) Direct dyes show a wide range of dyeing speeds on a given cellulose : the rapid dyeing dyes tend to yield level, and the slow unlevel, dyeings on material not possessing a uniform dyeing affinity.

Speed of dyeing is thus a very important factor both from a technological and a theoretical viewpoint. An examination of a comprehensive list of direct dyes [3] has shown that the rate of dyeing in similar conditions

[1] Boulton, Delph, Fothergill and Morton, *J. Textile Inst.*, **24**, P113, 1933.
[2] Neale, *J.S.C.I.*, **52**, 88T, 1933 ; Neale and Stringfellow, *Trans. Faraday Soc.*, **29**, 1167, 1933 ; Garvie, Griffiths and Neale, *Trans. Faraday Soc.*, **30**, 2, 1934 ; Hanson and Neale, *Trans. Faraday Soc.*, **30**, 386, 1934 ; Griffiths and Neale, *Trans. Faraday Soc.*, **30**, 395, 1934.
[3] Boulton and Reading, *J. Soc. Dyers and Col.*, **50**, 381, 1934.

covers a very wide range.  It is possible that the direct dyes differ more
widely in respect of this property than of any other.  In Table I. are

TABLE I.—Dyeing Behaviour of Some Direct Dyes on 150/27 * Viscose
AT 90°.[3]

| Dye. | Relative Dyeing Speed. | Approximate Diffusion Constant (cm.²/sec.). | Diffusion Constant Corrected for Absorption (cm.²/sec.). |
|---|---|---|---|
| Chlorazol fast Orange GS. . | 2200 | $4 \cdot 0 \times 10^{-8}$ | $2 \times 10^{-6}$ |
| Chrysophenine G. . . | 600 | $1 \cdot 1 \times 10^{-8}$ | $4 \times 10^{-7}$ |
| (C.I., No. 365) | | | |
| Sky Blue FF. . . | 9·8 | $1 \cdot 8 \times 10^{-10}$ | $7 \times 10^{-9}$ |
| (C.I., No. 518) | | | |
| Benzo fast Blue 8GL. . . | 2·6 | $4 \cdot 6 \times 10^{-11}$ | $2 \times 10^{-9}$ |
| Chlorazol fast Orange AGS. . | 1·0 | $1 \cdot 8 \times 10^{-11}$ | $7 \times 10^{-10}$ |

* A viscose yarn whose size is 150 denier and which is composed of 27 filaments
will be briefly described as 150/27 viscose.

given some velocity data for a few typical dyestuffs ranging from Chlorazol
fast Orange GS to Chlorazol fast Orange AGS, two dyestuffs which re-
present the extremes of fastness and slowness of those so far examined.
The dyeing speeds given in the second column are expressed as relative
to the speed of the slow dye Chlorazol fast Orange AGS.   By the assump-
tion of a formula for diffusion into a cylinder, given by Hill,[4] an approxi-
mate diffusion constant ($K'$) can be calculated from the kinetic data.
These values are given in the third column of Table I.   When it is
remembered that absorption of dye as well as diffusion is taking place
in the capillaries of the cellulose, it is clear that the value of $K$ is not that
actually applicable to the migration of dye in the capillary liquid.   Change
of concentration in any system is related to the diffusion constant by the
equation

$$\frac{dC}{dt} = K \frac{d^2C}{dx^2} \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

where $C$ is the concentration along an axis, $x$, $t$ is the time, and $K$ the
diffusion constant.
    In considering the case of diffusion of a solution along a capillary,
where the ratio of the amount absorbed on the walls to that in equili-
brium with it in the capillary fluid is $R$, it will be found that the diffusion
equation must be modified.   The following equations are found :—

$$\frac{dC'}{dt} = \frac{K}{R+1} \frac{d^2C'}{dx^2} \qquad . \qquad . \qquad . \qquad (2)$$
$$= K' \frac{d^2C'}{dx^2}$$

where $C'$ is a concentration term representing the total concentration of
solute absorbed as well as in solution, $K$ is the diffusion constant of the
solute in the capillary fluid, and $K'$ is the apparent diffusion constant for
the whole system.
    The dyeing of cellulose by a diffusion process approximates to this

[4] Hill, *Proc. Roy. Soc.*, **104B**, 39, 1928.

simple absorbing capillary system, so that the equations may probably be applied to the dyeing data with the object of calculating the order, if not the exact value, of the true diffusion coefficient of the dye in the capillary water of the cellulose.

In the dyeing experiments summarised in Table I., the value of $R$ was in each case approximately 40, so that, using this multiplier, the value of the true diffusion constant $(K)$ given in the last column can readily be calculated from the values of $K'$ in the third column.

Robinson and Hartley [5] have shown that, for several direct cotton dyes in water, the diffusion constant is near $5 \times 10^{-6}$ cm.$^2$/sec. at 25°: at 90°, the temperature at which the dyeing experiments were performed, the diffusion constant may be expected to be somewhat greater, of the order of $10^{-5}$ cm.$^2$/sec. A comparison of this value with those given in the final column of the table shows that the diffusion speed of the most rapid dyeing dyes within the cellulose capillaries, approaches that of the dye in free solution, whilst for the slow dyes the capillary diffusion may be ten thousand times slower than the free diffusion.

The understanding of these differences in the behaviour of the fast and the slow dyes can only come from a knowledge of the dimensions of the capillaries and the particles which have to traverse them. The data given by McBain and Kistler [6] for the permeability of a viscose sheet leads to the conclusion that the pores, through which the dye must pass in order to reach the interior of the dyed filament, are but a few atomic diameters in width. The possibility must therefore be considered that the difference in the ease of passage is due to differences in molecular size or shape of the dyestuffs. Amongst the first to notice the gradation in dyeing properties between the rapid and slow dyes, and to recognise its technical importance, were Wilson and Imison, [7] who advanced the suggestion that the slow, uneven-dyeing colours were distinguished by the possession of a relatively large molecular weight. Later experience has shown, however that there is no strict correlation between dyeing properties and molecular weight, although there is a general tendency for the dyes of higher molecular weight to be absorbed more slowly. Exceptions to the generalisation are numerous; thus Melantherine BH (Colour Index, No. 401, M.Wt., 803) dyes somewhat more slowly than Chlorazol fast Eosine B (Colour Index, No. 353a, M.Wt., 1072). [3] The molecular dimensions of the majority of the direct dyes of known constitution do not range widely; typical dyes are Chrysophenine G and Sky Blue FF whose molecules are $34 \times 7 \times 3$ Å.U. and $30 \times 9 \times 3$ Å.U. respectively. It is therefore probable that, for most dyes, molecular weight or size is directly a factor of secondary importance in influencing the dyeing speed, and indirectly an important factor only in so far as it influences the colloidal behaviour of the dye.

The direct dyestuffs are commonly stated in the literature to dissolve as colloidal micelles. The greater portion of the published data refers to solutions observed at ordinary temperatures, whilst the technically important temperature range in the dyeing of viscose cellulose is 70° upwards, where the colloidal behaviour of the dyestuffs is much less marked. It is probable, however, that even at the higher temperatures there is some aggregation of the dye molecules to some kind of micellar complex.

[5] Robinson and Hartley, *Proc. Roy. Soc.*, 134A, 20, 1931.
[6] McBain and Kistler, *Trans. Faraday Soc.*, 26, 157, 1930.
[7] Wilson and Imison, *J.S.C.I.*, 39, 322T, 1920.

There seems to be no reliable evidence as to the uniformity or other-wise of the micellar size of dissolved dyestuffs, but it is probable, *a priori*, that in a solution where micellar aggregation is taking place there will be particles whose sizes range from the simple molecule upwards, all in a state of dynamic equilibrium.

It is to be expected that the equilibrium in such a system will be displaced by a change in temperature, in the sense that a higher or lower temperature will favour a smaller or greater degree of aggregation respectively. After displacement the new equilibrium is probably attained within a few seconds at 70-100° and within a few minutes or hours at 20°. The experience of a very large number of quantitative dyeing experiments shows that no difference can be detected at the higher temperatures in the dyeing properties of two solutions of identical composition but differing history : the equilibrium is rapidly attained. At 20° it is sometimes possible to detect differences due to previous treatment. A dyebath, prepared from Benzopurpurine 4B (Colour Index, No. 448) and sodium chloride will dye viscose a little more rapidly at 20° when it has been recently heated to 100° and rapidly cooled than when it has remained, prior to dyeing, at 20° for a day.

Since the average size of the capillary channels within viscose cellulose is such that an aggregate of more than a few dyestuff molecules cannot enter for mechanical reasons, it follows that the whole course of dyestuff absorption depends on the presence of these small micelles. As these smaller particles are removed from the solution the equilibrium distribution of particle sizes will be disturbed and a fresh supply formed. According to this conception the kinetics of dyeing at higher temperatures will be controlled by the relatively slow speed of the diffusion process and the equilibrium concentration of small particles and not by the relatively rapid production of small particles to replace those absorbed by the cellulose.

Those dyestuffs which yield solutions rich in small particles may be expected to dye rapidly : with Chlorazol fast Orange GS (Table I.) it seems that at 90° all, or nearly all, of the solute is present in the dyebath as particles smaller than the cellulose capillaries. A dyestuff giving mainly large micelles on dissolution will dye slowly, for the whole diffusion process will be carried on by a small part of the solute.

The experimental work described in this paper has been undertaken to test this hypothesis of the relation of the colloidal structure of dye solutions to the fine structure of the dyed cellulose. Ultrafiltration experiments show that most dye solutions contain particles larger than the pores in normal regenerated cellulose, and that the slow dyeing dyes are relatively richer, compared with the rapid dyes, in large micelles.

## II. Fine Structure of Cellulose.

The general behaviour of cellulosic fibres and films has not yet been explained with complete satisfaction in terms of fine structure. X-ray investigation has yielded considerable information concerning the crystalline regions of the fibre, but these are not the only important structural element in the solid material. The size of these small regions of crystallinity may be estimated from the diffuseness of the X-ray diffraction pattern : Meyer and Mark [8] give the length as 150-200 Å.U. and thickness 40-50 Å.U.

[8] Meyer and Mark, *Ber.*, **61**, 365, 1928.

The general tendency of the X-ray crystallographers has been, until lately, to consider the crystallite as the unit of structure, and to build their structures from various arrangements of these discrete units.[9] This model does not account satisfactorily for the mechanical behaviour of cellulose, the imbition on wetting and the dyeing properties.

Haworth's [10] formulation of the cellulose molecule as a long chain of cellobiose residues is now generally accepted, and it has been shown, by chemical means, that this chain in cotton cellulose contains at least 100 of such residues.[11] The length of the molecular chain is therefore not less than 1000 Å.U., a value much greater than that obtained for the length of the crystallite.

The fine structure of an oriented cellulose is probably best imagined as a three-dimensional network of more or less parallel molecular chains, which are not necessarily straight since free rotation is possible at every glucosidic linkage, and which here and there fall into regions of crystalline arrangement. One molecular chain may thus be a member of more than one crystallite. In the intercrystalline regions the molecular chains are not bound together by strong crystal forces, so that they may move apart during swelling under the action of osmotic forces. Imbibition will continue until the osmotic forces are balanced by the elastic forces set up by deformation of the system. X-ray investigation shows that the crystalline regions remain unchanged during swelling in water : these regions then are the essential links which prevent disruption of the whole structure on swelling.

Since the crystalline regions are not penetrated by water of imbibition it follows that the molecular chains in this region are not subject to chemical attack by the usual agents and are not important in the absorption of dyes. It is in the amorphous intercrystalline region that the molecular chains are readily accessible to foreign molecules, and it is here, very probably that absorption of dye and chemical attack take place.

In an unswollen viscose film or fibre the molecular chains are fairly closely packed, for it can be shown experimentally that relatively small molecules cannot penetrate to the interior of the material. This fact can be demonstrated by some simple experiments. It has been shown by Kistler [12] that if cellulose is first swollen in water, the water may successively be replaced by miscible liquids. For example the water may be replaced by acetone or alcohol, and these by such a solvent as xylene. Working with the system cellulose-alcohol two extremes of imbibition may be attained : the first by plunging oven-dry, and the second wet, cellulose into an excess of alcohol. In the first state the cellulose is almost entirely unswollen and in the second almost as swollen as in water. Some measurements of the swelling of viscose, obtained by centrifuging the treated yarn for 5 minutes at 3000 r.p.m. in closed tubes [13] are shown in Table II. The

TABLE II.—IMBIBITION OF 150/27 VISCOSE YARN.

| Treatment. | Imbibition (g./g. Dry Yarn.) |
|---|---|
| Water . . . | 0·85 |
| Alcohol, swollen . | 0·44 |
| Alcohol, unswollen . | 0·11 |

[9] Meyer and Mark, *Der Aufbau der hochpolymeren organischen Naturstoffe* Leipzig, 1930.
[10] Haworth, *Helv. Chim. Acta.*, **11,** 534, 1928.
[11] Haworth, *Nature*, **129,** 365, 1932.
[12] Kistler, *J. Physical Chem.*, **56,** 32, 1932.
[13] Meunier and Guyot, *Rev. gén. Colloid*, **7,** 53, 1929.

results are typical of the behaviour of viscose cellulose in all forms, although the absolute magnitude of the swelling may vary distinctly. Sheet viscose is usually found to have an imbibition of approximately 1·2 and is therefore somewhat more permeable in the swollen form than viscose yarn generally.

The two preparations in alcohol show interesting differences in behaviour. An alcohol soluble substance with relatively small molecules, such as picric acid, will diffuse rapidly through sheet cellulose in the swollen state, but is completely retained by a sheet in the unswollen state. Again, swollen viscose yarn will absorb from alcoholic solution any sufficiently soluble direct dye, but is, in general, completely unstained in the unswollen condition. These observations are in harmony with those of McBain and Kistler,[6] who found it impossible to use sheet cellulose as an ultrafilter for organic solvents unless in the swollen state.

In the unswollen state the cellulose chain molecules in the intercrystalline regions are then sufficiently closely packed to prevent the passage of alcohol or picric acid molecules. The capillary spaces are less than $c.$ 5 Å.U. in diameter. As the cellulose swells by imbibition the structure becomes more permeable and the molecular chains move apart.

It should be noted that these remarks on fine structure and permeability apply only to viscose in the form of yarn or sheet, and not to cuprammonium rayon and natural cellulose—cotton, ramie, linen—whose permeability behaviour shows that the cellulose structure is penetrated by capillary spaces even in the unswollen condition.

The importance of swelling in the dyeing of viscose cellulose is clear. Unless there is a certain degree of swelling the dyestuff molecules cannot penetrate the structure : above this limiting swelling it seems probable that the greater the swelling, that is the wider the capillaries, the more rapidly will the dyeing process occur. This has already been shown to be the case for viscose yarn.[1] Treatment of the cellulose with sodium hydroxide solution increases the swelling and the dyeing speed, but leaves the equilibrium absorption of dye unchanged.

Knowledge of the size of the capillary spaces between the cellulose molecular chains is clearly desirable. In the very similar case of the nitrocellulose ultrafilters this has been found by two methods [14] which depend on the observation of either the critical pressure required to force air through a wet filter or the rate of filtration of water.

The first method tends to give the size of the larger pores, and the second a mean value. In the older type of nitrocellulose ultrafilters a wide range of pore sizes in the same membrane was obtained, but Elford [15] has shown by means of delicate biological tests that a very uniform filter is obtained if the conditions of coagulation are carefully controlled. The films so obtained have no observable microscopic structure. The uniformity in pore size of membranes prepared under conditions of uniform coagulation has also been demonstrated by a combination of the two methods of size determination,[16] the statistical distribution of pore size being found. It is very probable that viscose cellulose is, similarly, very nearly isoporous, since its coagulation is very regular.

McBain and Kistler,[6] using the critical gas pressure method, have concluded that the pore radius of sheet viscose (Duponts 600 Cellophan) is 20-30 Å.U.

[14] Bechold, *Z. physikal. Chem.*, **64**, 328, 1908.
[15] Elford, *J. Path. Bact.*, **34**, 505, 1931.
[16] Erbe, *Kolloid-Z.*, **63**, 277, 1933 ; Pisa, *Kolloid-Z.*, **63**, 139, 1933.

This value has been confirmed by a computation of pore size from a determination of the rate of flow of water through viscose membranes.

The apparatus employed was a water-jacketted funnel of a type similar to Zsigmondy's ultrafilter, constructed of brass. The membrane was a carefully washed sample of sheet viscose—Courtaulds' Viscacelle—about 0·0025 cm. in thickness. The permeability of this sheet and of material treated with sodium hydroxide solution of various strengths, was determined for distilled water at 20°. It was found an advantage to avoid the use of water which had been stored in glass vessels, and to use a sample which had been distilled directly into a stainless steel container. Blocking of the membrane, as shown by a diminution in filtration rate, was thereby reduced considerably.

The treatment with sodium hydroxide solution was for 15 minutes at 20°, followed by washing in water, dilute hydrochloric acid, water, dilute ammonia and finally twice with distilled water. The membranes after treatment must be preserved immersed in water, for the original imbibition is never regained after drying (see Table III.). Immersed in water the degree of swelling of the various membrane preparations remained constant for several weeks.

The imbibition of viscose, measured by centrifuging, after such treatment with sodium hydroxide is illustrated by the data, shown in Table III., for 150/40 viscose yarn.

TABLE III.—MODIFICATION OF IMBIBITION OF WATER BY 150/40 VISCOSE ON TREATMENT WITH NaOH.

| Concentration of NaOH. | Imbibition ($H_2O$ g./g Dry Yarn). | |
|---|---|---|
| | Undried. | After Drying at 105° for 90 Minutes. |
| 0·0 per cent. | 0·95 | — |
| 1·0 ,, | 1·02 | 0·90 |
| 2·0 ,, | 1·09 | 0·94 |
| 4·0 ,, | 1·20 | 0·98 |
| 6·0 ,, | 1·40 | 1·06 |
| 8·0 ,, | 2·50 | — |

The behaviour of sheet cellulose, with and without pretreatment with sodium hydroxide solutions, with respect to permeability to water is summarised in Table IV.

TABLE IV.—PERMEABILITY OF SHEET CELLULOSE TO WATER AT 20° UNDER A PRESSURE OF 70 CM. OF MERCURY.

| Treatment. | Imbibition of $H_2O$ g./g. Cellulose. | $w$. | wt./cm.$^2$ (mg.). | $t \times 10^3$ (cm.). | $D$. | $r$ (Å. U.). | $\beta$ (Å. U.). |
|---|---|---|---|---|---|---|---|
| 0 % NaOH | 1·30 | 0·65 | 5·7 | 4·7 | 0·047 | 15·2 | 6·6 |
| 4 % ,, | 1·74 | 0·74 | 7·1 | 5·9 | 0·077 | 20·0 | 8·7 |
| 6 % ,, | 1·94 | 0·76 | 7·7 | 6·6 | 0·089 | 21·5 | 9·3 |
| 8 % ,, | 2·65 | 0·81 | 9·0 | 7·8 | 0·210 | 34·2 | 14·7 |
| 10 % ,, | 4·62 | 0·88 | 10·6 | 9·8 | 1·19 | 94 | 41 |
| 10 % ,, | 4·35 | 0·88 | 9·7 | 9·0 | 0·89 | 78 | 34 |

The imbibition of the wet films was measured by drying quickly between sheets of filter paper, weighing, drying at 105°, and reweighing ; from this figure the water content $w$, in c.c. water per c.c. of membrane, may be calculated. In the fourth column of the Table the wet weight of a square cm. of the film is recorded, and from this was calculated the thickness, $t$, of the membrane in the wet condition. The permeability of the membrane, $D$, is expressed as the quantity of water passed by one square cm. each hour for one atmosphere excess pressure.

Bjerrum and Manegold [17] have published a full discussion of the mathematical treatment of the results of such filtration experiments with capillary material. They have shown that from such experimental data as that given in Table IV. it is possible to calculate the size of the capillaries for various types of structure. Two of the structural types are of interest in the interpretation of the data relating to gels of cellulose and similar materials, namely those in which capillaries of circular cross-section and parallel sided cracks, respectively, are randomly oriented. The equations connecting the capillary size with the experimental values are :—

$$r = \sqrt{24 \cdot q \cdot t \cdot \eta / w} \qquad . \qquad . \qquad . \qquad . \quad (3)$$

$$\beta = \sqrt{4 \cdot 5 \ q \cdot t \cdot \eta / w} \qquad . \qquad . \qquad . \qquad . \quad (4)$$

where $r$ and $\beta$ are the radius of the circular capillaries and the semi-width of the parallel sided cracks respectively, $q$ is the permeability of the membrane in c.c./cm.²/sec./dyne, $\eta$ is the viscosity of the fluid being forced through the membrane in absolute units, and $t$ and $w$ are the thickness and the water content of the membranes as before defined.

In the last two columns of Table IV. values of $r$ and $\beta$ are given for the various membranes. Current conceptions of the structure of cellulose make it appear probable that in this material the capillary spaces have a conformation intermediate between the two ideal structures employed for the purposes of computation.

TABLE V.—SUCCESSIVE DETERMINATIONS OF PERMEABILITY ON A MEMBRANE OF SHEET CELLULOSE PRETREATED WITH 10 PER CENT. NaOH. $T = 20°$.

| Determination. | Pressure (P). | Permeability (A) c.c./cm.²/hr. | 100 A/P. |
|---|---|---|---|
| 1 | 60 cm. Hg | 0·71 | 1·18 |
| 2 | 40 ,, | 0·47 | 1·18 |
| 3 | 20 ,, | 0·25 | 1·25 |
| 4 | 10 ,, | 0·135 | 1·35 |
| 5 | 60 ,, | 0·67 | 1·12 |
| 6 | 10 ,, | 0·130 | 1·30 |
| 7 | 60 ,, | 0·65 | 1·08 |

It is probable, therefore, that the average diameter of the capillary pores in the sheet cellulose employed in this series of experiments is approximately 20 Å.U. The pore size in the usual viscose yarns will be somewhat smaller than this, for viscose yarn exhibits usually a smaller imbibition and dyeing speed than this sample of viscose sheet.

The permeability of viscose film follows fairly closely the behaviour expected from this ideal hydrodynamical model. There is, however, a slight diminution in the permeability with increase of pressure applied, probably related to a slight decrease in imbibition. In addition the permeability of a given film slowly diminishes with the amount of water filtered, probably because of mechanical clogging of the filter by fine suspended matter. These two points are illustrated by the data of Table V.

TABLE VI.—VARIATION IN PERMEABILITY OF A VISCOSE SHEET WITH TEMPERATURE.

| Temperature. | Permeability (D). | Viscosity ($\eta$). | $D \cdot \eta$. |
|---|---|---|---|
| 20° | 0·79 | 0·0100 poise | 0·0079 |
| 80° | 2·5 | 0·00356 ,, | 0·0089 |

The permeability of the material increases with temperature to an extent explained by the diminution in the viscosity of water. The effect of temperature of permeability is shown in the data given in Table VI. Heating to 80° causes no great change in the structure of the film. The

[17] Bjerrum and Manegold, *Kolloid-Z.*, 43, 5, 1927.

capillary dimensions found for viscose at 20° will therefore be valid also for viscose immersed in a dyebath at the usual dyeing temperatures, 70°-100°.

The relation between average pore size and swelling is shown in Fig. 1.

## III. Ultrafiltration of Dye Solutions.

Numerous experiments have been recorded on the ultrafiltration of dye solutions; in general they show, in agreement with other methods, that in solutions of the direct cotton colours there is considerable aggregation of molecules to micellar complexes. The majority of the experiments seem to have been carried out at laboratory temperatures, and no record has been found of ultrafiltrations of dye solutions performed in the temperature range 70°-100°. In order to relate the colloidal behaviour of the direct dyes with their dyeing properties it is essential that ultrafiltration experiments designed to this end should be carried out at the higher temperatures used in the dyeing process.



FIG. 1.—Variation in pore size of sheet cellulose with degree of swelling.

At the commencement of the ultrafiltration experiments an attempt was made to employ the usual nitrocellulose membranes prepared from an ether-alcohol collodion. The nitrocellulose films used had, from a calculation similar to that already detailed for viscose films, an average pore diameter of 150-200 Å.U.

When an attempt was made to filter solutions of Sky Blue FF containing 0·005 per cent. of the dye and various amounts of sodium chloride it was found that the filtrate was quite colourless, both at 75° and 20°, even when a considerable volume of solution had been passed through the membrane. This effect is probably due to adsorption of dye by the membrane, for it was found that Sky Blue FF showed, even in the absence of salt, a very considerable affinity for the films employed. Similar effects were noted for other direct dyes. A second difficulty in the use of nitrocellulose filters is that their structure is not stable at 70°-80°. It was found that membranes used at these temperatures, or heated in a bath of water, showed a steady diminution in permeability and consequently in average pore size. This change in membrane properties has been noted by Elford in sterilisation by heat.[15]

For these reasons the use of nitrocellulose films was discontinued and viscose films substituted. These films are stable at 100°, and, although in solutions containing sodium chloride absorption of dye by the membrane occurs, this absorption seems to be less than that noted with the nitrocellulose membranes.

It is clear that the membrane most desirable in experiments directed to the relation of colloidal and dyeing properties, is one in which the pore size approximates to the pore size in the material as generally dyed. That is, it is desirable to employ untreated viscose sheet. Unfortunately the rate of filtration with such a membrane for the maximum pressure, 45 cm. of mercury, which could be applied is too small for practical use. The membranes actually employed were those which were given a preliminary swelling at 20° for 15 minutes in 2·5 normal sodium hydroxide solution, and which had a pore diameter, calculated by means of equation 3, of near 180 Å.U. This pore size was found sufficiently small to show differences between the solutions of the several direct dyes used, and large enough to give a convenient filtration rate.

The solutions were maintained at 75° by means of hot water passed through the jacket of the funnel, and it was found possible to maintain a temperature constant within ± 2°. In working with the brass funnel it was found that interaction between the metal and the dye solution could be completely eliminated for several dyes by lightly silvering the whole apparatus. With the four dyes employed in the ultrafiltration experiment no indications whatsoever of interaction between solution and metal were noted.

The dyes employed, Sky Blue FF, Chrysophenine G, Chlorazol fast Orange AGS, and Benzo fast Blue 8GL, were all purified by repeated salting out with sodium acetate followed by extraction with alcohol.[18] Analysis showed the first two dyes to be chemically pure.[1] With regard to the other two dyes, analytical methods are useless since the molecular constitution is not generally known, but the method of purification makes it certain that they are free from the usual diluents, and their dyeing behaviour suggests that they are chemical individuals. It may be assumed therefore that the samples of all four dyes actually employed were substantially pure. Reference to Table I. shows that these dyes have a wide range of dyeing speeds. Two other purified dyes, Chlorazol fast Orange GS, and Icyl Blue G, were also used in the ultrafilter, but, owing to some interaction of solution and apparatus, a certain amount of precipitation of dye occurred, and the results were therefore discarded.

TABLE VII.—FILTRATION OF 0·005 PER CENT. DYE SOLUTIONS THROUGH A VISCOSE MEMBRANE OF CAPILLARY DIAMETER 180 Å.U.

| Dyestuff. | Tempera-ture. | Concentration of Filtrate (Per Cent. of Original Solution). | | | | | |
|---|---|---|---|---|---|---|---|
| | | Concentration of NaCl in Solution. | | | | | |
| | | 0 Per Cent. | 0·005 Per Cent. | 0·025 Per Cent. | 0·10 Per Cent. | 0·50 Per Cent. | 2·5 Per Cent. |
| Chrysophenine GS . . | 75° | 44 | 54 | 96 | 95 | 95 | — |
| Sky Blue FF . . . | 20° | 1 | 10 | 26 | 27 | 26 | 15 |
| ,, ,, ,, . . | 75° | 15 | 16 | 33 | 82 | 93 | 80 |
| Benzo fast Blue 8GL. . | 75° | 3 | — | 34 | 67 | 70 | 62 |
| Chlorazol fast Orange AGS. | 75° | 10 | — | 26 | 59 | 55 | 48 |

[18] Robinson and Mills, *Proc. Roy. Soc.*, **131A**, 596, 1931.

The membranes at both 20° and 75° filtered dye solutions at the same rate as water. A 0·5 per cent. solution of picric acid and a 0·1 per cent. solution of sodium aminoazobenzene-monosulphonate were filtered without change in the concentration of solute.

The concentration of the solutions of direct dyes employed was 0·005 per cent., a value which was chosen as approximating to that of a normal dyebath, and with each dye a series of solutions containing various concentrations of sodium chloride, from 0-5 per cent., were filtered.

The filtrate was invariably at first colourless, but later showed the presence of dye. Usually when 2 c.c. per square cm. of membrane had been filtered the absorption of dye on the membrane had reached an equilibrium value, and the concentration of dye in the filtrate attained constancy. After this point had been reached a sample of filtrate was collected and analysed colorimetrically for dyestuff.
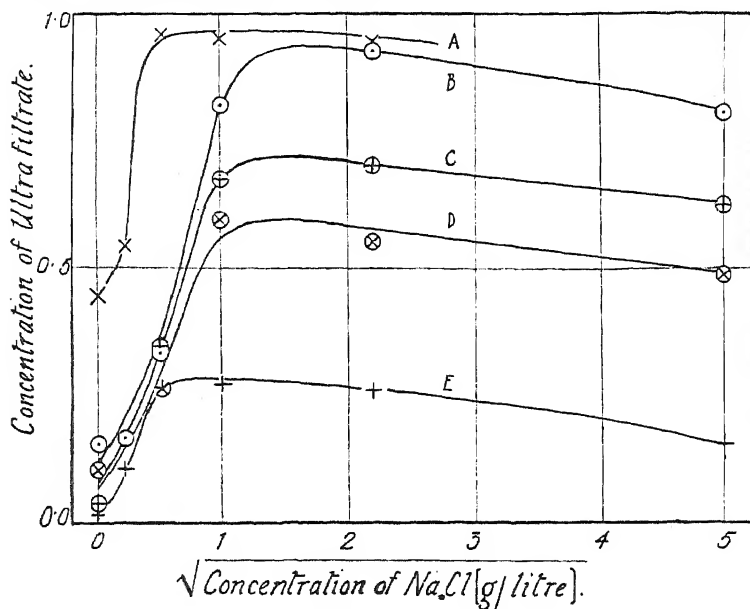


FIG. 2.—The variation in concentration of ultrafiltrate, relative to the filtered solution, with salt concentration.

A Chrysophenine G at 75°.    D Chlorazol fast Orange AGS at 75°.
B Sky blue FF at 75°.    E Sky blue FF at 20°.
C Benzo fast blue 8GL at 75°.

The results of the series of experiments are set out in Table VII. and given graphically in Fig. 2.

The following conclusions concerning the colloidal states of the dye solutions may be drawn from the data :—

(a) At 75° all the solutions contain aggregates which do not pass through capillaries whose approximate diameter is 180 Å.U.

(b) The proportion of large particles is greatest for all the dyes investigated in the absence of sodium chloride. With increasing amounts of sodium chloride the dispersion of the dye passes through a maximum and then slowly decreases. Such an effect of small amounts of salt have previously been reported for several colloid systems. For example Wo. Ostwald [19] has put forward evidence to show that Benzopurpurine 4B has

[19] Wo. Ostwald, *Trans. Faraday Soc.*, **29**, 347, 1933.

a maximum solubility in the presence of a certain concentration of sodium chloride.

(c) With Sky Blue FF the dispersion of the dye is much greater at 75° than at 20°.

(d) At 75° the solutions of four dyestuffs used show similar behaviour with respect to addition of salt, but they may be arranged in a well-marked order of increasing maximum dispersion, namely, Chlorazol fast Orange AGS, Benzo fast Blue 8GL, Sky Blue FF, Chrysophenine G.


## IV. Discussion.

The experimental evidence presented in the last two sections shows that the capillary spaces in viscose cellulose are of the same order of size as dyestuff molecules, and further that the direct dyes are dissolved col·loidally, to some extent, at 75°. The dyeing process is thus somewhat of a paradox.

The difficulty may be resolved by regarding a colloidal dye solution not as a dispersion of micelles of long life and fixed size, but as in a state of equilibrium between molecular aggregating forces and thermal dis·persing forces. In a dye solution there will be particles of all sizes, from the single molecule upwards, and the effect of a change of conditions, such as temperature or salt content of the solution, will be to displace the equilibrium to a new distribution of particle sizes.

Some indication of this type of system can be obtained by the fol·lowing treatment of a special case. Two assumptions are made :—

1. The micelle is filamentary in form with the constituent molecules lying side by side. Such a micellar form is probable for many dye solu·tions since they form gels, give filamentary coagulates, and show stream·ing double refraction and dichroism.

2. There is a constant probability, $a$, that one side of a given mole·cule terminates a micellar complex. The probability that it is united to another in a micelle is therefore $1 - a$.

In a micelle composed of $n$ molecules, there will be 2 ends and $n - 1$ molecular linkages. The probability of such a structure is :—

$$a^2 (1 - a)^{n-1}$$

Since there are $n$ component molecules, the probability of solute occurring in this form is $n$ times this value. The amount of dissolved material in each size group, for unit amount of solute, is therefore :

|  |  |  |  |
|---|---|---|---|
| Single molecules | . | . | $a^2$ |
| Aggregates of 2 molecules | | | $2a^2 (1 - a)$ |
| ,, | 3 | ,, | $3a^2 (1 - a)^2$ |
| ,, | $n$ | ,, | $na^2 (1 - a)^{n-1}$ |

The distribution of particle size, for several values of $a$, is shown in Fig. 3. Although the assumptions employed in this treatment probably do not correspond to actuality, yet it is probable that the equilibrium in any micellar system is qualitatively similar to the foregoing ideal equilibrium. In a dye solution possessing a mobile equilibrium it may be expected, no matter what the average aggregation is, that there is a finite concentration of solute dispersed molecularly or as very small · molecular aggregates, and a maximum in the dispersion curve at a particle size depending on the tendency to aggregation. The greater the ten·dency to aggregation, the smaller will be the relative concentration of

particles of molecular size, and the greater the particle size corresponding to the maximum in the dispersion curve.

In the absorption of such a colloidal solute by a capillary substance it is clear that only those particles smaller than the pore size will be active in the transport of the solute within the solid. The effect of such a filtration on the rate of absorption may be seen from a further consideration of equation 2 :

$$\frac{dC'}{dt} = \frac{K}{R + 1} \cdot \frac{d^2C'}{dx^2}.$$

In applying this equation to the estimation of a diffusion constant corrected for absorption it was assumed that the concentration of dye in the capillary water was that in the external solution. The concentration in the capillaries is, however, dependent on the proportion of small
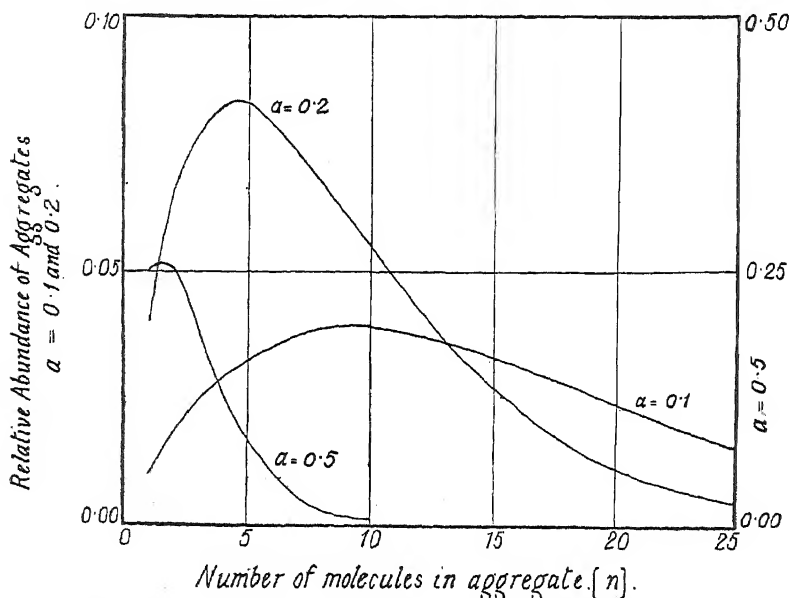


FIG. 3.—The distribution of micellar sizes in an ideal type of aggregating solution.

particles present, and is in general less than in the solution. The real value of $R$ is therefore greater than that assumed. Now for a given value of the true capillary diffusion constant, $K$, the greater the value of $R$, the smaller will be the value of the observed diffusion constant, $K'$, for the whole absorbing system. The effect, then, of decreasing the proportion of small particles in a dye solution is to cause a decrease in the apparent diffusion constant, $K'$, that is in the speed of dyeing.

The true diffusion constants for all direct dyes are probably of the same order, so that it is to be anticipated that those possessing the greatest degree of aggregation and the smallest concentration of small particles will be the slow dyeing dyestuffs.

This is confirmed by the ultrafiltration experiments quoted in section III. The order of dyes in decreasing dyeing speed, Chrysophenine G, Sky Blue FF, Benzo fast Blue 8GL, and Chlorazol fast Orange AGS, is also the order of increasing colloidality. Further, the variation in

colloidality with salt for a single dye is related to the dyeing properties in the same way. Neale and his colleagues [2] have shown with several direct dyes that the rate of dyeing varies with the sodium chloride content of the dye solution : as the salt concentration increases from zero the dyeing speed rapidly increases to a flat maximum and then decreases. The low value of the dyeing speed in the presence of small salt concentrations may probably be assigned to the greater tendency to aggregation, and consequent poverty in small particles, in such solutions, as is shown by the ultrafiltration experiments. The diminution in the dyeing speed at higher salt concentrations is almost certainly due to the greater absorption of dye, and consequent increase in the value of $R$ (equation 2), in such systems.

The hypothesis which has been outlined provides a means of correlating a number of observations which have been made in a study of the direct dyeing process. In the succeeding paragraphs it will be shown that a number of these generalisations are capable of qualitative explanation in terms of cellulose structure and dispersion of dye solution.

The rate of diffusion of a given direct dye within viscose is not a constant. Not only is there a wide range of permeabilities amongst viscose yarns of different preparations, but also with a single viscose sample modified by various treatments. In general it may be stated that a high degree of orientation of the crystallites and a low imbibition on wetting with water are factors which make for a low dyeing speed. Thus treatment of a sample of viscose yarn by drying at 140°, or with a solution of sodium hydroxide, yields preparations dyeing slower or faster, with imbibitions smaller or greater, respectively, than the original material. It appears that speed of dyeing varies in the same sense as size of the capillary channels in the cellulose. A series of viscose samples of differing permeability, when dyed with a polydisperse solution of the type discussed above, may be expected to show characteristic differences in relative dyeing speeds with solutions of differing states of aggregation. With a very even dyestuff, where there is little colloidal aggregation, the range of dyeing speeds with different viscoses will not be great, since most of the particles in every case are able to enter the capillaries. With a slow-dyeing colour an increase in the capillary dimensions will admit an increased number of dyestuff particles and so will produce an increase in the dyeing speed. It is to be anticipated, therefore, that the relative difference in dyeing speed between two different preparations of viscose will be greater with the slow than with the rapid dyeing direct dyes. The behaviour of viscose has been found experimentally to agree with this expectation.[1] A corollary to this generalisation is that the range of dyeing speeds between the slow and rapid dyeing colours will be less extended for a permeable than for a slow dyeing preparation of viscose. Here again observation and expectation coincide.

Temperature is found to have an unexpectedly large effect on the speed of dyeing of viscose. Thus it has been found, for a 150/27 viscose, that there is a 50-fold increase in absorption velocity between 55° and 90° in the case of Sky Blue FF. This large temperature speed coefficient is almost certainly connected with the decrease in colloidality with increasing temperature, demonstrated, in the case of Sky Blue FF, by the ultrafiltration data of Section III.

The extent of aggregation in a dyestuff solution represents a balance between a tendency to dissolve in molecular form and a tendency of the molecules to unite with one another to form micelles. With the rapid

dyeing colours the former tendency, and with the slow dyes the latter tendency, clearly predominates. It is probable that co-ordinate linkages between polar groups are the bonds which not only unite the molecules in the micelles but also bind the dye molecules to the cellulose chains, so it is to be expected that a direct dye in which the co-ordinating is more important than the dissolving tendency will not only give a solution with a high degree of aggregation, but also be strongly absorbed by cellulose. Confirming this Neale [2] has found that, in general the slow dyeing dyestuffs have a higher saturation absorption on viscose than the rapid dyestuffs.

The mechanism which has been postulated for the direct dyeing of cellulose has probably been based on an over-simplified model, for no account has been taken of such factors as variation in capillary size, the diminished rate of diffusion of molecules or particles having dimensions approximately the same as those of the capillaries traversed, surface migration of adsorbed molecules, and the possible blocking of capillaries by large particles. In spite of this, however, it is believed that the hypothesis as stated provides a means of correlating qualitatively a mass of data on the dyeing of cellulose hitherto without adequate explanation.

## Summary.

(1) The fine structure of viscose cellulose is shown to possess, in the unswollen state, a pore diameter of less than 5 Å.U., and in the normal swollen state 20-30 Å.U. This value may be increased 5-fold by swelling in sodium hydroxide solution. Experiments in an alcoholic medium show that direct dye molecules can only penetrate the capillaries in the swollen state.

(2) The rate of diffusion of the most rapid dyeing of the direct dyes within the cellulose capillaries approaches that for free diffusion in water ; that for the slowest dyes is $10^{-4}$ of this value.

(3) Ultrafiltration experiments, using cellulose membranes, show that the degree of aggregation is greater with the slow dyeing than with the rapid dyeing colours.

(4) A solution of a direct dye probably contains aggregates of molecules of all sizes from a single molecule upwards. A probable distribution of particle sizes has been indicated, and it is shown that the dyeing kinetics to be expected of such a solution are essentially those observed in the dyeing of viscose.

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## GENERAL DISCUSSION.

**Mr. J. Boulton** (*Braintree*) said : In Table I. of Dr. Morton's paper there appears a list of approximate diffusion constants calculated from data recorded elsewhere.[1] I have recently determined diffusion constants ($K$) for Sky Blue FF diffusing from a 0·005 g./100 c.c. solution

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[1] J. Boulton and B. Reading, *J. Soc. Dyers Cols. In the press.*

into a cylinder of regenerated cellulose (viscose) under a variety of conditions. This value, calculated by means of the diffusion formula of A. V. Hill[2] is found to vary, at 90° C., between $1 \cdot 10 \times 10^{-10}$ and $4 \cdot 00 \times 10^{-10}$ cm.$^2$/sec. according to the concentration of added sodium chloride. The approximate figure calculated by Dr. Morton is seen to lie between these values. In order to obtain $K$ by application of Hill's formula to experimental rate-of-dyeing data, it is, of course, necessary to maintain a constant concentration of dyestuff in the solution from which absorption is taking place. The data used for the value of " $K'$ " given in the paper were obtained by experiments in which this concentration was reduced by 50 per cent. by the process of absorption. This circumstance does not seem to have affected the order of the value of " $K'$ ".

With regard to the variation of the speed of dyeing, as expressed by a diffusion constant, I find that $K$ reaches a maximum with increasing concentration of sodium chloride and then decreases. The same effect has been noticed by Neale and his co-workers[3] for diffusion of a number of dyes into plane viscose sheet, although their results give diffusion constants for Sky Blue FF of an order ten times greater than those obtained for a cylindrical viscose yarn. There is no ready explanation for the increase in speed of diffusion with increase in electrolyte concentration ; the various data, presented at this meeting, on free diffusion of dye bodies into water and solutions of electrolytes, reveal no factor which might assist in explaining the maximum in the diffusion constant-salt concentration relationship which has become evident in experiments in diffusion of the same dye bodies into cellulose.

**Dr. Conmar Robinson** (*London*) said : I cannot believe that small quantities of sodium chloride will *increase* the degree of dispersion of pure dyes. It is, however, *possible* that, if certain impurities were present, an increase in the degree of dispersion might be found which may account for such claims having been made in the past.

I think, however, there is a more probable explanation of Dr. Morton's results. Neale and his co-workers found, by means of very careful quantitative work, that certain substantive dyes do not dye viscose at all in the complete absence of salt. I believe that the explanation of this is as follows. Viscose has a negative charge and this charge being of the same size as that of the dye, opposes the adsorption of the dye. The *first* action of small additions of electrolytes is to suppress the influence of this charge, which would be done by a few millimols of sodium chloride per litre.

Similarly, I suggest that the negative charge in the viscose capillaries opposes the passage of the dye, but that in the presence of 1 gm. per litre of NaCl (say 15 millimols per litre) the effect of the charge will be almost completely suppressed and hence the dye will pass more readily. In other words, the chief effect of the salt is in altering the properties of the filter and any effect on the degree of dispersion of the dye will be of secondary importance.

**Dr. T. H. Morton** (*Braintree*) said : Dr. Robinson has suggested that the negative charge on cellulose is the cause of two different effects, namely, a zero equilibrium absorption of certain dyes such as Sky Blue FF in the absence of salt, and a diminution in the concentration of the ultrafiltrate.

[2] A. V. Hill, *Proc. Roy. Soc.*, **104B**, 39, 1928.
[3] S. M. Neale and others, *Trans. Faraday Soc.*, **29**, 1167, 1933 ; **30**, 271, 1934 ; **30**, 386, 1934.

Actually it is found that with, say, Sky Blue FF, there is a slight negative absorption of the dye, for the dye solution is concentrated somewhat by the immersion of the dry yarn : proportionately more water than dye is absorbed by the viscose.   It seems preferable to regard this phenomenon as due to a mechanical rather than an electrical effect, for it is difficult to see how the $\zeta$-potential on cellulose can appreciably modify the equilibrium absorption of, or combination with, electrically neutral dye molecules, although it might possibly influence the speed of attaining this equilibrium.   The negative absorption of Sky Blue FF by viscose in the absence of salt is probably best explained by the small degree of combination of cellulose and dye under these conditions, to-gether with the exclusion of the larger dye particles from the cellulose capillaries.

The second point of Dr. Robinson that the $\zeta$-potential is of great importance in controlling the diffusion of dyestuffs into viscose is prob-ably negatived, so far as single molecules are concerned, by the evidence given in the paper that dilute solutions of sodium aminoazobenzene-monosulphonate are passed in undiminished concentration by viscose membranes.   The molecule of this dye is of the same general character as those of the direct dyes studied, but of approximately half the size of the latter.

**Dr. Conmar Robinson** said : I think that both these points can be explained by the same theory.   The fact that Neale in some cases found a negative adsorption of dye in the absence of salt is as would be ex-pected if the negative charge repels the dye micelles sufficiently.   Dr. Morton's second point is that some low molecular weight dyes have the same degree of ultrafiltrability, irrespective of the salt concentration. The effect of the charge that I predict would only be significant where the pore size is sufficiently small with respect to the dye.   Dr. Morton *chose* filters with a pore size that would give sufficient differences in the ultrafiltrability of the dyes used.   If, however, we then take a dye of much lower molecular weight (and lower micellar weight) such as sodium aminoazo-benzene monosulphonate, the effect of the charge may be so small that it will not appear in the filtration results.

**Professor H. Freundlich** (*London*) : I would like to add to Dr. Robinson's remarks that there are cases known where the diffusion of an ion through a membrane is distinctly and undoubtedly influenced by the electrical charge on the walls of the capillaries of the membrane, anions being strongly retarded by a negative charge, cations by a positive one.[4]

**Dr. E. Valkó** (*Ludwigshafen a/ Rh*) said : Referring to the earlier important publications of Neale and co-workers on the one side, Boulton, Delph, Fothergill and Morton on the other side, I have made in my paper some remarks about the relationship between particle size and dying process.   Dr. Morton's new paper gives us a welcome opportunity of dealing with this question briefly again.   I am glad to observe that a proposition which I made in my paper was superfluous, because it has now been carried out by Dr. Morton.   That proposition was to take into account, in the calculation of apparent diffusion coefficients of dyes in cellulosic material, the fact that a part of the dye is absorbed—in analogy to the consideration of Hill in the fourth chapter of his quoted paper. I have, however, some doubts whether the use of a constant partition coefficient is satisfactory.   We are also in complete agreement in our

[4] *Cf.* Michaelis, *Naturwiss.*, **14**, 33, 1926 ; see also Bikerman, *Kolloid Z.*, **62**, 26, 1933.

view that the part of dye dissolved which in dying penetrates the cellu-losic material is probably only the finest, or molecularly dispersed part.

Comparing my values for the diffusion coefficient with the filtration results of Dr. Morton, we notice a striking, but, as we shall indicate, only an apparent discrepancy. We find, for the radius of Sky Blue FF (which is identical with Chicago Blue 6B) in the NaCl solution of 0·002-0·5$N$ at 25° the values 9·55-17·5 ÅU. Morton finds, however, that a membrane of a pore diameter of about 90 ÅU. retains 73-99 per cent. of the same dyestuff, if it was filtered from a solution with a NaCl content of 0-0·4$N$. A consideration indicates, however, that the pore diameter which is hydrodynamically determined is many times larger than the diameter of the smallest particle against which the membrane acts as a sieve. The streaming rate gives a certain value for the average cross-section area of the pores, while the sieve effect is only determined by the most constricted part of the single channel.

Bechold[5] said : " Sieve experiments . . . especially with bac-teria, proved that the pore diameter able to let through a germ must be 8-15 times as large as itself."

The results obtained by Dr. Morton are in accordance with this statement.

The second question which I wish to discuss is the variation in con-centration of ultrafiltrate with salt concentration, demonstrated in Fig. 2, and Table VII. in Dr. Morton's paper. The assumption of the existence of a maximum dispersion of dye with increasing salt concentration is often made, but the arguments in its favour are very scarce. In my paper I report about the degree of association of three substantive dyes in the presence of NaCl in the concentration 0·01-0·5 $N$. The association number always increases with increasing salt concentration. The fact that the maximum values of Dr. Morton lie at lower salt concentrations does not imply any direct contradiction between the two experiments. Nevertheless, I prefer to suggest that the variation in the passing of the dye across the membrane is influenced rather by the change of the permeability properties of the membrane than by the variation of the dispersion degree of the day. On the basis of the water permeability of a certain collodion membrane, Manegold[6] calculates for its pore radius the following values :

(1) In water . . . . $r = 24·9$ m$\mu$.
(2) In 0·1 $N$ NaCl . . . $r = 29·0$ m$\mu$.

He suggests that the change is the consequence of the variation of eletrokinetic potential at the surface of the pore wall. The same obser-vation has already been made by Duclaux and Errera.[7]

As a matter of fact, the important observation of Dr. Morton, that the substantive dyes are capable of passing the pores of cellulosic material at most in a very slight degree, is independent of these considerations.

**Professor E. Elöd** (*Karlsruhe*) said : It may be interesting to point out that not only the colloidal electrolytes but also crystalloids in the velocity of their action on cellulose fibres depend to a great extent on the swelling degree of the cellulose fibres. Together with Dr. Schmid-Bielenberg[8] I was recently able to point out that cotton, ramie, hemp

[5] Bechhold, Schlesinger and Silbereisen, *Koll. Z.*, **55**, 172, 1931.

[6] Manegold, *Koll. Z.*, **61**, 140, 1932.

[7] Duclaux and Errera, *Revue gen. coll.*, **2**, 130, 1924 ; **3**, 97, 1925.

[8] E. Elöd and H. Schmid-Bielenberg, *Z. physik. Chem.*, **25B**, 27, 1934,

and flax in an air-dry condition show in the stated sequence a decreasing velocity of acetylation, *i.e.* that with those fibres, which in the stated sequence show increasing orientation of their crystallites, as X-ray analysis proves, possess increasing hindrances to diffusion even when exposed to crystalloid dispersed agents. However, if these fibres are left to swell, for instance, with water these diffusion hindrances will disappear and with an optimal swelling degree of about 20 per cent. water, a distinct increase on the one hand of acetylation velocity takes place. On the other hand, the differences caused by the fine structure of the fibres disappear also and all the above-mentioned natural cellulose fibres show the same velocity of acetylation.

We must not forget to mention that, in addition, the velocity of the taking up of substantive dyestuffs by these kinds of fibres corresponds also to the above-mentioned sequence. In substantive dyeing, too, one can on the other hand by previously swelling the fibres with water extensively equalise and destroy the hindrances to diffusion.

Finally, I may ask how cuprammonium rayon reacts in substantive dyeing, compared to viscose, it being well known that cuprammonium rayon possesses a larger inner surface and owing to the gentler conditions of coagulation is not so extensively superficially blocked (for instance, by hemicellulose or destruction products of the cellulose) as viscose.

**Dr. T. H. Morton** (*Braintree*) said : Dr. Valkó is undoubtedly correct in stating that the use of a partition coefficient in the calculation of diffusion constants is not completely satisfactory, but it is believed that, failing a complete mathematical solution of the complex problem of diffusion with absorption, it does present a method of arriving at an approximate value for the apparent rate of migration of dye within the absorbing system.

A factor must be applied to a pore diameter determined hydrodynamically in order to calculate a value for the maximum size of particle passed by the membrane, and Dr. Valkó quotes biological evidence favouring a factor of $1/8$-$1/15$. Later work, however, suggests that this value should be nearer unity. W. J. Elford [9] gives values of $1$-$1/3$, but since he employs an equation based on parallel capillaries running from one face of the membrane to the other affording a value of $r\sqrt{3}$ times smaller than that employed in the paper (equation 3), these become $\frac{1}{2}$-$1/5$. The results obtained by Elford with ultrafilters and those by Bechold with the ultracentrifuge have been compared (see table).[10]

| Organism. | Diameter in $m\mu$. | |
| --- | --- | --- |
| | Centrifuge. | Filter. |
| Smallpox vaccine | 200 | 125–175 |
| Chicken plague | 110 | 60–90 |
| Bacteriophage WL | 90 | 50–75 |
| ,,  D20 | 50 | 20–30 |
| ,,  S13 | 20 | 8–12 |

It seems, therefore, that for these organisms, which are apparently spherical, the use of the above filtration factors has given values for particle size which are somewhat too low. The most probable value for the correction factor for the viscose membranes employed, having a hydrodynamic capillary diameter of 180 ÅU, is $1/3$-$1/5$.

[9] *Proc. Roy. Soc.*, 112B, 384, 1933.
[10] H. Bechold, *Kolloid-Zeitschr.*, 66, 329 ; 67, 66, 1934.

Such a correction factor will, however, be of use only in the derivation of particle size in the case of spherical particles. Experiments with streaming solutions have shown that the micelles of many direct dyestuffs depart very greatly from spherical form, so that it is difficult to draw quantitative conclusions of the degree of dispersion of their solutions from ultrafiltration data, although semi-quantitative comparisons should be possible. The deviation of the dyestuff micelle from a spherical form is possibly demonstrated by the values given by Dr. Valkó for the particle diameter of Benzopurpurine 4B, Congo Red, and Sky Blue FF, which are often smaller than the long axis of the dye molecules, approximately 30 ÅU.

Professor Elöd has stressed the fact that in general a reagent must penetrate the capillary spaces of cellulose before reacting. In this connection it is interesting to compare the behaviour of the natural fibres, cotton, ramie, and linen, with that of viscose. It is found whilst viscose does not, the natural fibres do absorb a direct dye from alcoholic
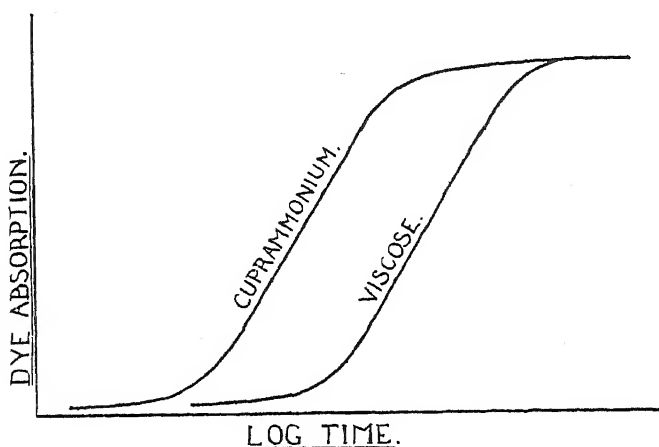


ABSORPTION OF DYE BY VISCOSE AND CUPRAMMONIUM RAYONS.

solution in the unswollen state. The natural fibres appear to have a less regular fine structure than viscose, possessing capillary pores sufficiently large to admit dye molecules when the fibre is in the unswollen state. This structure is lost when cotton is mercerised under tension, the cellulose then approaching viscose in its behaviour towards alcoholic dye solutions.

Cuprammonium rayon in its behaviour to such alcoholic solutions seems to possess a fine structure somewhat similar to the natural cellulosic fibres. The capillaries in cuprammonium are probably larger than in viscose, the two forms of cellulose being related in the same way as a permeable and an almost impermeable collodion ultrafiltration membrane. The dyeing behaviour of the two rayons towards an aqueous direct dye solution containing salt is shown schematically in the figure. The equilibrium absorptions are similar, and the kinetics of dyeing differ only in a velocity constant, the cuprammonium dyeing much more rapidly than the viscose yarn.

**Mr. G. S. Hartley** (*London*) enquired, in connection with the

measurements on the rate of dyeing, whether it would be possible for diffusion into the pores of a membrane to be interfered with by a cyclic convection process within the pores due to endosmosis.  If we had a system of interconnected pores of different diameters in a material giving rise to a $\zeta$-potential and diffused into them a salt giving rise to a diffusion potential, endosmosis would try to occur and would succeed in the smaller pores at the expense of the larger ones.  Viscose is negatively charged with respect to water and the dyes used are anionic :  consequently the endosmotic pressure would be directed *towards* the dyeing solution and the cyclic convection would tend, therefore, to keep the dye out of the smaller pores.  If, as is probable, the smaller pores are much more numerous, their total surface might be greater than that of the larger pores, and the endosmosis would therefore tend to decrease the rate of dyeing.  The addition of salt would lower the normal diffusion velocity of the dye but would also decrease the endosmosis, and if the latter effect outweighed the former, an increased rate of dyeing would result, as had been found by Neale.

**Dr. S. M. Neale** (*Manchester*) (*communicated*) :  I rather doubt whether Dr. Morton's ultra filtration experiment, using cellulose membranes, really proves any more than our original observation that the rate of diffusion into cellulose at first increases with increasing concentration of added electrolyte.  On account of the fact that the membrane is far from inert towards the diffusing substance, its use as an ultra filter may be attended with complications due to adsorption.  Personally I would rather incline towards Dr. Robinson's suggestion that the foreign electrolyte first acts by suppressing the charge on the membrane.

It is difficult to be dogmatic with regard to the importance of degree of aggregation in dyeing with direct cotton colours.  The careful experiments of Robinson and his co-workers have shown how very difficult it is to obtain trustworthy values for the degree of aggregation, even at the ordinary temperature.  The evidence so far available, however, seems to show relatively slight aggregation, and my own personal view is that at the elevated temperatures used in our own experiments (usually 90° C.) aggregation of the dyestuff is of little or no importance, except perhaps at exceptionally high concentrations of added electrolyte, approaching flocculation point.

I agree with Dr. Valkó's suggestion that some distinction should be made between free and adsorbed dye in the membrane, and that Morton's assumption of a constant partition coefficient is not altogether satisfactory.  Nor is the treatment in the fourth part of Hill's paper, where the case considered is one in which the diffusing substance is being used up at a constant rate by chemical reaction *in situ*, directly applicable to the diffusion of dye into cellulose.

Mr. W. M. Garvie, working in collaboration with me, has recently been making measurements of the diffusion of dyestuffs through cellulose membranes, and has also analysed the process of diffusion into a mass of cellulose made up of fourteen separate membranes.

A preliminary consideration of his results shows that the simple diffusion equation can only be regarded as a first approximation.  Any definite statement would be premature, but it appears that a more correct representation of the facts may be obtained by the use of equation

$$-\frac{dS}{dt} = k\frac{\alpha C'}{\alpha x},$$

where $S$ represents the total dye (both free and adsorbed) passing a plane $x$ cms. from the surface, and $C'$ represents the concentration of dyestuff in the liquid phase in equilibrium with cellulose containing the concentration of dye $(C)$ actually present at the point $x$. The relation between $C$ and $C'$ is found by a series of experiments in which the equilibrium absorption is determined for a suitable range of values of the concentration of dye in the solution.

In reply to Dr. Valkó's query concerning the absorption of dye by cupra rayon, we have examined this point and find that whether in the form of filament or sheet, cupra rayon absorbs more dyestuff than viscose, and moreover gives a higher coefficient of diffusion.

The relation between the two forms of cellulose varies, however, with the concentration of electrolyte present. The available information will be put forward for publication very shortly.

The effect of the foreign electrolyte in increasing the equilibrium absorption of dyestuffs by cellulose, could possibly be explained by the application of the principles of Donnan Equilibria. If we assume that only the dyestuff anions $(R^-)$ are bound by the cellulose, whereas the corresponding $Na^+$ ions are free to take part in ionic equilibria, then it follows that if $R^-$ is absorbed by cellulose the concentration of $Na^+$ ions must be greater in the cellulose phase than in the aqueous phase.

The concentration of *free* $R^-$ ions in the cellulose phase will therefore be much less than in the external solution according to the equation

$$\frac{[R^-]_1}{[R^-]_2} = \left(\frac{[Na^+]_2}{[Na^+]_1}\right)^n = \lambda < 1.$$

If now we add a neutral electrolyte such as NaCl, the value of the ion partition factor $\lambda$ becomes nearer unity, and so the concentration of free $R^-$ ion in the cellulose phase is increased. The amount of dye absorbed therefore increases, since it is in equilibrium with the free dye concentration.

The crucial proof of this theory would lie in the analysis of the distribution of $Cl^-$ ion between the two phases, but we have not yet found it possible to do this.

Identical conclusions as to the effect of NaCl can also be reached quite simply on a thermodynamic basis, regarding negative dyestuff ions as the absorbable components. The idea that only neutral dyestuff molecules $Na_nR$ can be absorbed, and the application of the Law of Mass Action to determine their concentration, naturally also leads to a rather similar result.

**Dr. T. H. Morton** (*communicated*) : In the discussion, Professor Freundlich, Dr. Robinson, Dr. Valkó, and Mr. Hartley have all laid stress on the importance of the electrokinetic factor in the dyeing of cellulose. It is probable, however, that this factor is of relatively small importance, and that the dyeing process is conditioned mainly by mechanical factors.

It has been suggested that the increase in speed of migration of dye and in concentration of ultrafiltrate on the addition of small quantities of salt to the system is due to the action of the latter in diminishing the $\zeta$-potential. This electrokinetic potential has its origin in the few carboxylic groups occurring in the cellulose structure ; in the presence of salt, dye molecules are absorbed and effectively become part of the cellulose structure, increasing the number of its ionogenic groups and therefore its charge. The effect of salt is thus simultaneously to increase the total

negative charge on the cellulose structure and to reduce the electro-kinetic importance of the charge. It seems difficult to draw any *a priori* conclusion as to the variation in the $\zeta$-potential in the cellulose-dye system on addition of salt.

It is well known that the addition of certain organic substances to the system is capable of increasing very greatly the rate of diffusion of dyestuff through the cellulose when the addition has probably little or no effect on the electrokinetic properties of the material. Examples of slightly acidic and slightly basic, almost neutral additional substances are $\rho$-naphthol and pyridine. The probable mode of action of these substances is an alteration of the colloidal condition of the dye. As a concrete example, the desorption of viscose dyed with Sky Blue FF into water and aqueous pyridine media containing no salt may be considered. In water the dye is stripped very slowly, but much more quickly in aqueous pyridine. It is difficult to conceive of any electrokinetic explanation of the slowness of diffusion of the dye within cellulose in the first case which is not equally valid in the second instance where the diffusion is comparatively very rapid.

A direct test of the part played by the negative charge on cellulose in modifying the dyeing process is perhaps to be found in the study of the dyeing behaviour of those *basic* dyes which have an affinity for cellulose, and which are also apparently colloidal in aqueous solution. Examples of such dyes are Union Red (Colour Index, No. 266) and Union Brown A (Colour Index, No. 535) in which the solubilising group is a fully substituted ammonium chloride, giving a positive charge to the particle, in contrast to the sulphonate group and the negative charge of the direct dyes.

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# PART II. (C) SILICATES AND SILICIC ACID.

# SOME ELECTROCHEMICAL PROPERTIES OF COLLOIDAL SILICA.

By V. A. Kargin and Adolph J. Rabinovitch.

## 1. General Survey of the Problem.

Pure silicic acid sols have been in recent years the object of numerous investigations. A detailed study was made of their electro-chemical properties and the relations of the latter to the stability of the sols.

However the results of many such investigations seem strange in themselves and moreover are seriously contradictory.

Thus, in the investigations of Pauli and Valkó [1] and Rabinovitch and Laskin [2] who studied electro-dialysed $SiO_2$ sols prepared according to Graham and Grimaux,[3] potentiometric and conductometric determinations of the hydrogen ion concentration showed a very high acidity. The comparison of these concentrations with the total amount of hydrogen ions determined according to Pauli's [4] method : *viz.* conductometric

[1] Wo. Pauli and E. Valko, *Kolloid Z.*, **36**, *Erg. Bd.* 325, 1925; **38**, 289, 1926.
[2] A. J. Rabinowitsch and E. Laskin, *Z. physikal. Chem.*, **134**, 390, 1928.
[3] E. Grimaux, *C.R.*, **98**, 105, 1884.
[4] Wo. Pauli and A. Semler, *Kolloid Z.*, **34**, 145, 1924.

titration with alkali, enabled us to determine the " degree of dissocia-
tion " " $\alpha$ " or the " activity factor " $f_a$ for these sols which also proved
to be very high.   In the investigation of Rabinovitch and Laskin it
approximates to 91 per cent. and in the investigations of Pauli and Valkó
—100 per cent.

According to the conception of Pauli and Valkó all potentiometrically
determined hydrogen ions in a colloidal system act as compensating ions
(Gegenionen), i.e., are situated in the outer component of the electrical
double layer surrounding the colloidal particles.

They regard the anions $HSiO_3^-$ or analogous ions of polysilicic acids
as the " charging ions " (aufladende Ionen) creating the charge on the
colloidal particles.   If this conception is correct these acids must be re-
garded as extremely strong acids totally dissociated into ions.

Proceeding from analogous considerations Rabinovitch and Laskin [2]
calculated in their paper the dissociation constants of such acids and
found that they are not lower than $2 \times 10^{-4}$.   Mukherjee [5] and co-
workers found also that colloidal silicic acid, owing to some of its pro-
perties, must be placed among strong acids and, according to others,
among weak ones.   As shown in our first paper [6] the assumption of
Pauli and Valkó tacitly accepted by other authors and according to which
potentiometric measurements enable us to determine the concentration
of compensating ions entering the double layer is erroneous.   The col-
loidal particle being in a state of thermodynamical equilibrium with
the surrounding solution the potentiometrically determined activity
of the ions of the peptising electrolyte must remain unchanged from
the surface of the colloidal particle down to the depth of the intermicellar
liquid where no more traces of the double layers are to be found.   Let
us denote this position as the " zero point."   The decrease of the ionic
concentration with the increase of the distance from the particle must be
compensated by the increase of the activity factor reaching the value
$f_a = 1 \cdot 00$ at the " zero point."   Therefore the potentiometric deter-
mination gives, properly speaking, only the concentration (equal to the
activity) of the peptising electrolyte ions at the " zero point " of the
intermicellar liquid and cannot possibly give any information as to the
concentrations of the ions in the double layer, as their distribution and
consequently the spatial distribution of the activity factor remains un-
known up to the present time.

From this standpoint the potentiometrically found high hydrogen
ion concentrations in silicic acid sols show the presence of a strong acid
in the intermicellar liquid of these sols.

On the other hand a serious discrepancy can be traced between the
group of investigations showing colloidal silicic acid to be a strong acid [1, 2, 5]
as compared with the same acid in true solution,[2] and those stating that
by polymerisation of the acid from true solution up to the colloidal state
its electrolytic dissociation constant remains unchanged [7] or even de-
creases.[8]   According to Brintzinger and Troemer,[7] in obtaining colloidal
silicic acid by different methods, the first stage of the process is invariably
the true solution of silicic acid which with time passes through all stages
of polymerisation up to the formation of colloidal particles.   This was

[5] J. Mukherjee, Kolloid Z., 67, 178, 1934.
[6] See this Discussion, p. 50.
[7] H. B. Brintzinger and B. Troemer, Z. anorg. allg. Chem., 181, 234, 1929.
[8] R. Willstätter, H. Kraut and K. Lobinger, Ber., 61, 2280, 1928 ; 62, 2027,
1929.

demonstrated by the change of the refraction and diffusion property. Based on this we should expect the electrochemical properties of colloidal silica prepared by various methods (that of Graham, that of Grimaux, of Willstätter,[8] etc.) to be similar, if we assume that the resulting $SiO_2$ sols are absolutely pure and can be described by Pauli's scheme. But as shown above they are extremely different.   Further, it seems very difficult to account for the stability minimum of $SiO_2$ sols with changing $p_H$ found by Flemming,[9] and carefully examined by Freundlich and Cohn [10] and Ray and Ganguly.[11]   These authors demonstrated that silicic acid sols (very stable in acid and strongly alkaline solutions as to the addition of electrolytes) grow very unstable in the range of $p_H = 9 \cdot 5$ to 11 according to the data of Freundlich and Cohn or in the range of $p_H = 6$ to 9 according to Ray and Ganguli.   Freundlich and Cohn account for this stability minimum by the dehydration of the colloidal particles of silicic acid in presence of alkali.

Finally, serious contradictions exist between the scheme of the acid silica sols structure proposed by Pauli and Valkó and the processes called forth by the addition of electrolyte solutions to these sols.

According to Pauli and Valkó the structure of these sols may be represented by the following schematic formula :

$$[x(SiO_2 + nH_2O) . y . SiO_3H^-] + yH^+ \qquad . \qquad . \quad (\text{I})$$
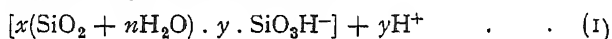
When electrolyte solutions are added it would be natural to expect the appearance of exchange adsorption : *viz.* the adsorption of the cation of the added electrolyte by the colloid particles and the equivalent displacement of $H^+$ ions out of the double layer into the intermicellar liquid.

However, a series of investigations showed that, contrary to what is known for silica gel,[12] no exchange adsorption is observed in acid silica sols.   Laskin [13] in our laboratory stated that the addition of salts causing the coagulation of $SiO_2$ sols (*e.g.*, $CaCl_2$) of the basic dyes which are adsorbed in the coagulation of $SiO_2$ sols, does not acidify the sols.

Pauli and Valkó proposed their above-mentioned scheme for acid silica sols prepared according to Graham by mixing sodium silicate with hydrochloric acid, according to Grimaux by hydrolysis of methylsilicic ester, or according to Ebler and Fellner [14] by hydrolysis of silicon tetrachloride and subsequently purified by energetic electrodialysis in order to remove the impurities and the electrolytes formed during the process of the preparation of the sol : NaCl in the first method and HCl in the last one.

Pauli and Valkó suppose that the $SiO_2$ sols purified in this manner are actually pure silicic acid sols answering their scheme of an "ideal colloidal electrolyte " : all charging ions (anions of silica or polysilicic acids) are situated on the surface of the colloidal particles, all the hydrogen ions resulting from the dissociation of the surface molecules of the silicic acids form the outer component of the double layer and are determined in potentiometrical measurements.

For the alkaline sols of silicic acid obtained by addition of alkali to

[9] W. Fleming, *Z. physikal. Chem.*, **41**, 427, 1902.
[10] H. Freundlich and H. Cohn, *Kolloid Z.*, **39**, 26, 1926.
[11] R. C. Ray and P. B. Ganguly, *J. Physic. Chem.*, **34**, 352, 1930.
[12] S. Glixelli, *C.R.*, **176**, 1714, 1924; S. Glixelli and J. Wiertelak, *Kolloid Z.*, **43**, 85, 1927 ; **45**, 197, 1928 ; J. Mukherjee *et al.*, *J. Chem. Soc.*, **129**, 3023, 1926.
[13] E. Laskin, *Kolloid Z.*, **45**, 129, 1929.
[14] E. Ebler and M. Fellner, *Ber.*, **44**, 1111, 1915.

acid sols they assume an analogous scheme differing from the first one only as far as the hydrogen ions are partially or totally substituted by sodium.

$$[x(SiO_2 + nH_2O) \cdot ySiO_3H^-] + yNa^+ \qquad . \qquad . \quad (2)$$
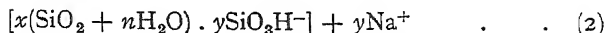
According to this conception the gradual increase of alkalinity of acid $SiO_2$ sols should result in an uniform transition in all the properties of the sols, among them the adsorption property and the stability. Indeed, a pure $SiO_2$ sol in which for instance 90 per cent. of the hydrogen ions are substituted by sodium should be almost the same as to its adsorption properties as the alkaline sol, notwithstanding that its $p_H$ value is as low as 5. Similarly its stability should increase uniformly with the addition of alkali, which, as pointed out above, is not actually observed.

All these considerations made us doubt the validity of the scheme of colloidal silica structure advanced by Pauli and Valkó,[1] and accepted in one of the previous papers from our laboratory.[2] Many of the contradictions stated above could be settled if it were shown that the high acidity of the silica sols, particularly of those having an acid reaction, is due not to the dissociation of colloidal silica, as a " colloidal electrolyte " according to Pauli, but to an admixture of a common acid in true solution which is distributed between the particles and the intermicellar liquid.

The same may be inferred from the investigations of Jordis,[15] Jander[16] and Lottermoser[17] with co-workers, who showed that acid $SiO_2$ sols, thoroughly purified from electrolytes (acids) by electrodialysis, lose their stability or even cannot be obtained in the absence of a stabilising electrolyte (acid). In order to verify this idea and to elucidate the problem of the electrochemical properties of colloidal silicic acid a series of experiments was carried out in our laboratory—a brief account of which will be given in the present paper.

## 2. Preparation of Pure Silica Sols by Electrodialysis and their Electrochemical Properties.

In the first investigation made by A. J. Bybaev (Baibaev), we endeavoured to obtain the purest possible silica sols free from electrolytes in order to study their electrochemical properties and to find out the origin of the high H ion concentrations in sols previously investigated.

With this purpose $SiO_2$ sols were prepared by hydrolysis of silicon tetrachloride. A stream of dry air saturated with $SiCl_4$ vapours was passed through ice-cooled, twice distilled water having the specific conductivity of $1·2 \times 10^{-6}$ mho. The sols obtained were aged for several days and afterwards purified by dialysis in collodion sacs against distilled water.

After dialysis the sols were submitted to electrodialysis. Platinum gauze electrodes and parchment paper membranes were used in the apparatus. These membranes were soaked in twice-distilled water for 3 days and were then carefully purified by electrodialysis in the same apparatus, the inner cell being consecutively filled with $5 \times 10^{-4}$ N. NaOH, HCl and KCl-solutions and finally with pure twice-distilled water. The outer cells contained ordinary distilled water which was changed twice a day. In the last run pure twice-distilled water was filled into the whole apparatus and electrodialysis continued for 15 to 20 hours more. After this the

[15] E. Jordis, *Z. anorg. Chem.*, **44,** 200, 1905.
[16] G. Jander and W. Heukershoven, *Z. anorg. allg. Chem.*, **201,** 361, 1931.
[17] A. Lottermoser and H.-J. Kiehn, *Kolloid Beihefte*, **35,** 123, 1932.

electrical conductivity of the liquid in the inner cell remained constant for several days under the potential and without it.

The apparatus being purified in this manner, dialysed silica sols were introduced into the inner cell and submitted to electro-dialysis under gradually growing potential difference from 35 to 445 volts for several days with interruptions from 13 to 40 hours.   In this process the conductivity of the sols decreased rapidly at the first, then more slowly and finally became constant.   This constancy held under the potential and after long interruptions.   It is remarkable that the final *conductivity* of silica sols *was equal to* that of pure twice-distilled " electrolytic " *water*, amounting only to $1 \cdot 2 \times 10^{-6}$ mho.

Determinations of $p_H$ in such sols, made with platinum hydrogen electrodes yield somewhat unreliable values, similar to those in pure water. Potentiometric titration with alkali using a $Pt/H_2$ electrode points also to the absence of acids in the sol.

The extremely pure $SiO_2$ sols obtained were thus electrochemically neutral and their H ion concentration did not exceed that of purest laboratory water.   This seems to indicate that acid $SiO_2$ sols used in the investigations by previous authors and by ourselves [2] were insufficiently freed from electrolytes, mainly HCl.   This has been indirectly confirmed by the following experiments.   Many of our sols did not stand prolonged electrodialysis and coagulated in the inner cell.   On being taken out after long purification such gels were readily peptised by hydrochloric acid (final concentration $0 \cdot 01 - 0 \cdot 1$ $N$.).

### 3. Preparation and Investigation of Pure $SiO_2$ Sols from Silane.

In addition to silica sols purified by electrodialysis we obtained silicic acid sols free from electrolytes owing to the method of preparation.   For this purpose silane, silicon tetrahydride $SiH_4$ was oxidised by ozone in water.
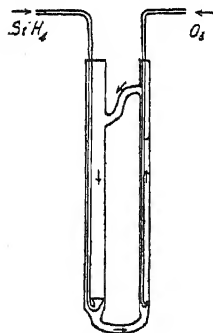
$SiH_4$ was obtained according to Stock and Somiesky [18] by treating magnesium silicide $Mg_2Si$ by HCl.   $Mg_2Si$ was made according to Gattermann [19] using the reaction of powdered magnesium with pure precipitated silica.   The initial materials were checked for the absence of As and P.

Electrolytic hydrogen is carefully purified by passing through a wash tube with a $CaCl_2$-solution, an electrically heated tube containing palladised asbestos, $CaCl_2$ again and a glass coil cooled by liquid air, enters then the round flask in which the decomposition of $Mg_2Si$ by HCl is effected and carries the generated $SiH_4$ away to the oxidation vessel.   On its way the gaseous mixture passes 4 scrubbers containing water in order to be freed from HCl (preliminary experiments have shown that complete purification is attained after passing the second scrubber) and a coil cooled in carbon dioxide with acetone for the freezing out of higher hydrosilicons.

FIG. 1.

The oxidation vessel (see Fig. 1) consists of two vertical glass tubes of Jena *Geräteglas* 20, 55 cm. in height, connected at their lower and upper parts.   Into the tube having the larger diameter (4 cm.) enters the $SiH_4$ inlet tube which ends in a porous glass filter plate.   The tube bearing ozonised electrolytic oxygen enters the other tube of the oxidation vessel of lower diameter (2 cm.).   When running both gases through such a system with equal velocity, owing to the difference in diameters we obtain a circulation of the liquid which is marked by arrows on the figure.   Thus

[18] A. Stock and C. Somiesky, *Ber.*, 49, 111, 1916.
[19] L. Gattermann, *Ber.*, 22, 186, 1922.

water in the oxidation vessel is saturated by ozone. $SiH_4$ enters through the porous glass filter in small bubbles and is oxidised to $SiO_2$. A considerable part of the silica forms a coarse suspension, a part of it forms a slightly opalescent yellow colloidal solution. This colour is obviously due to traces of silicon which is liberated in the process of oxidation of higher hydrosilicons.

The $SiO_2$ sols with 0·2 g./l. obtained do not possess any acid properties, nor do the electrodialysed sols. $p_H$ determinations with a platinum-hydrogen electrode give values near $p_H$ 7. Curves of potentiometric titration are similar to those of the above described sols.

Thus, we come to the conclusion that pure sols of silicic acid are electrochemically neutral, do not possess acid properties and only a small quantity of compensating ions (*Gegenionen*) in the outer component of the double layer, which is indeterminable by electrometric methods.

The stability of these sols is probably due only to the lyophilic properties of silicic acid.

At the same time it is known that strong acids, *e.g.*, HCl produce a stabilising action upon $SiO_2$ sols : the sols become more stable when acidified and $SiO_2$ gels may be directly peptised by HCl. As shown by Lösenbeck,[20] with increasing concentration of HCl in $SiO_2$ sols the negative charge of the latter increases, passes a maximum, then decreases again. At HCl concentrations of $10^{-2}$ to $10^{-3}$ N. reversal of the sign occurs. This might be explained in such a manner that in sols of lower acidity more $Cl^-$ ions are adsorbed on colloidal particles than $H^+$ ions, in more acid sols the opposite takes place. Thus H ions play the part of compensating ions in negative sols, $Cl^-$ ions in the positive ones.

## 4. Measurements on Highly Acid $SiO_2$ Sols.

This could be verified if the values of $p_H$ and $p_{Cl}$ were measured in a series of dilutions of highly acid $SiO_2$ sols ($p_H < 2$). With increasing $p_H$ the reversal zone has to be passed, and the nature of the compensating ions must change. At this point the intersection of the $p_H$ dilution and $p_{Cl}$ dilution curves has to be observed.

Such a series of experiments on highly acid (slightly dialysed) $SiO_2$ sols was conducted in our laboratory by A. J. Bybaev. The $p_H$ determinations were made using a $Pt$-$H_2$ electrode, the $p_{Cl}$-measurements using a calomel electrode, both against saturated calomel electrodes.



FIG. 2.

In separate experiments the total amount of HCl in the sol was determined by two parallel titrations—by alkali with a $Pt$-$H_2$ electrode and by $AgNO_3$ using a silver electrode. The position of the inflection points coincided on both curves. Similar results were obtained on two other $SiO_2$ sols with various HCl contents. This is an indication that all titrated $H^+$ and $Cl^-$ ions belong to the hydrochloric acid and support the above conclusion that the quantity of true compensating ions in acid $SiO_2$ sols is very small.

The results of these measurements are given in Fig. 2.

The $p_H$ dilution (1) and $p_{Cl}$ dilution (2) curves are nearly linear, do not

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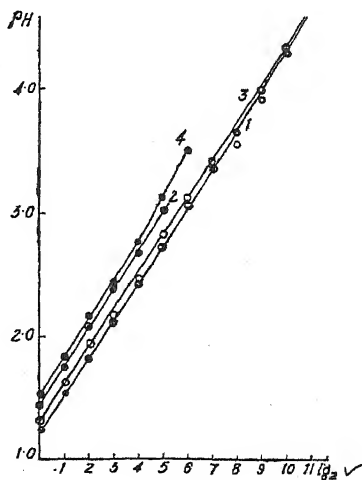
[20] O. Lösenbeck, *Kolloid. Beihefte*, **16**, 27, 1922.

intersect and are nearly parallel over the whole range of measurements. As the calomel electrode is not very reliable in acid solutions, parallel measurements were made with solutions of pure hydrochloric acid ($p_H$ curve 3 ; $p_{Cl}$ curve 4), diluted in the same proportions as the sol. Straight lines were obtained which, within the limits of experimental error, check with the corresponding curves of the $SiO_2$ sol.

This showed once more that the potentiometrically determinable H$^+$ and Cl$^-$ ions in silicic acid sols are not compensating ions (*Gegenionen*) but are present in the intermicellar liquid as HCl. The amount of true compensating ions as well in negative as in positive $SiO_2$ sols is so small that it cannot be determined by the potentiometric method.

The readings of the calomel electrode being not very reliable under these conditions and the experimental errors high we could have failed to notice a small amount of compensating ions and that the more that with the dilution of the sol the amount of compensating ions decreases in the same proportion.

In order to avoid this error we made another series of measurements on $SiO_2$ sols with constant $SiO_2$ content and varying HCl content. In this series only the $p_H$ values were determined potentiometrically, conductivity determinations being substituted for $p_{Cl}$ measurements. Conductivity was calculated from the observed $p_H$ values, assuming that all H$^+$ ions belong to HCl, and the calculated $\kappa_{25}$ values were compared with the experimentally determined ones. See Table I.

TABLE I.

| Sol No. | $p_H$ | [H$^+$]. | $\kappa_{25}$ Calc. | $\kappa_{25}$ Exper. | $\Delta\kappa$. | $\Delta\kappa$ in Per Cent. |
|---|---|---|---|---|---|---|
| 2 | 1·51 | $3·09 . 10^{-2}$ | $1·27 . 10^{-2}$ | $1·19 . 10^{-2}$ | $+ 0·08 . 10^{-2}$ | $+ 6·3$ |
| 3 | 1·80 | $1·61 . 10^{-2}$ | $6·63 . 10^{-3}$ | $6·20 . 10^{-3}$ | $+ 0·43 . 10^{-3}$ | $+ 6·5$ |
| 4 | 2·60 | $2·57 . 10^{-3}$ | $9·84 . 10^{-4}$ | $9·92 . 10^{-4}$ | $- 0·08 . 10^{-4}$ | $- 0·8$ |
| 5 | 2·96 | $1·11 . 10^{-3}$ | $4·62 . 10^{-4}$ | $4·38 . 10^{-4}$ | $+ 0·24 . 10^{-4}$ | $+ 5·2$ |
| 6 | 3·65 | $2·14 . 10^{-4}$ | $9·03 . 10^{-5}$ | $9·11 . 10^{-5}$ | $- 0·08 . 10^{-5}$ | $- 0·9$ |
| 7 | 3·99 | $1·00 . 10^{-4}$ | $4·22 . 10^{-5}$ | $4·39 . 10^{-5}$ | $- 0·17 . 10^{-5}$ | $- 4·0$ |

As shown by this table, the discrepancies between the calculated and the observed conductivity values $\Delta\kappa$ do not exceed 6·5 per cent. of the conductivity value, *i.e.*, fall within the limits of the errors of observation and calculation. However the sign of the prevailing deviations has to be noted.

These data show again that the activity of the true compensating ions in acid $SiO_2$ sols is very small and cannot be determined by potentiometrical methods. Those ions which are potentiometrically discovered are not the compensating ions of the " colloidal electrolyte " but normal ions of the electrolyte admixed to $SiO_2$ sols. As shown in our first paper [6] this is characteristic not only of silica sols but also of a number of other negatively charged colloids.

## 5. Cataphoretic Measurements.

The data obtained showing very low amounts of compensating ions in acid $SiO_2$ sols made us believe that the corresponding values of electro-kinetic ($\zeta$-) potentials are also very low. Therefore A. Bybaev in our laboratory made an attempt to determine $\zeta$-potentials from cataphoretic measurements. Silica sols prepared from $SiCl_4$ and submitted to ageing in presence of HCl have a notable opalescence which enables to determine the cataphoretic velocity by the macroscopic method when observing the Tyndall-effect on the moving boundary. The measurements were made

in a Kruyt U-tube under the conditions discussed by Rabinovitch and Fodiman.[21]

Some of our $SiO_2$ sols showed a slight cataphoretic effect—the boundary moving towards the cathode or the anode 1 to 2 mm. for 5 to 6 hours under a potential drop of about 5 to 7 volt/cm.; but the majority did not move in the electric field at all. These sols contained HCl in concentrations from $10^{-4}$ to $10^{-1}$ N. No movement of the boundary could be noticed for 2 to 6 hours at potential drops of 3 to 9 volt/cm.

Thus the values of electrokinetic ($\zeta$-) potential obtained are very low or zero, in accordance with our data on the amount of compensating ions.

On the other hand the introduction even of very small amounts of trivalent salts largely increases the cataphoretic velocity of positive $SiO_2$ sols. The strongest effect is produced by $FeCl_3$; $AlCl_3$ acts more mildly, $TiO_2$ still less. This gives some reason to suppose that the high values of transference numbers found by Lösenbeck [20] for acid $SiO_2$ sols are to a large degree due to the presence of sesquioxides in the silica sols investigated by this author. This is also probably the cause of the poor reproducibility of the cataphoretic experiments and the determinations of transference numbers of $SiO_2$ sols.

We think that the investigations of Bybaev in our laboratory helped to understand the cause of the high acidity of "pure" silicic acid sols and of the high values of the dissociation constants of colloidal silica. Both effects can be readily explained if we take in account that a strong acid (mainly HCl) is always present in $SiO_2$ sols which can be completely removed from the particles only by electrodialysis under very severe conditions.

Moreover, the very small number of charges on the colloidal particles and of compensating ions around it shown in this paper provide an explanation of the absence of ionic exchange adsorption by acid silica sols, as found previously in our laboratory.[13]

## 6. Examination of a Previous Paper on $SiO_2$ Sols from our Laboratory.

In the light of these new results it is interesting to revise a previous paper on colloidal silica made in our laboratory by Rabinovitch and Laskin.[2]

In this investigation $SiO_2$ sols obtained according to Graham were dialysed and electrodialysed and concentrated by evaporation. Their $p_H$ values varied from 3·23 to 4·05. Data obtained by use of the hydrogen and the quinhydrone electrodes checked very well; hydrogen ion concentrations calculated using the formula of Pauli and Valkó: [1]

$$h_\kappa = \frac{1000\,\kappa}{u_H + v_{Koll.}} = \frac{1000\,\kappa_{25}}{350 + 20} = 2·70\,\kappa_{25} \quad . \quad . \quad \text{(P-V)}$$

gave certain deviations from the potentiometrically determined values, which however did not exceed 15·5 per cent.

If we make a new calculation of our previous experimental results not taking in account the concept of Pauli that acid silica sols are pure colloid electrolytes and assuming that all the measured hydrogen ions belong to hydrochloric acid in the intermicellar liquid, by use of the formula:

$$h_\kappa = \frac{1000\,\kappa}{u_H + v_{Cl}} = \frac{1000\,\kappa_{25}}{350 + 75} = 2·36\,\kappa_{25} \quad . \quad . \quad \text{(K-R)}$$

we get, instead of Table IV. of the previous paper, the following Table II.:

[21] A. J. Rabinowitsch and E. Fodiman. *Kolloid Z.*, **59**, 310, 1932.

TABLE II.

| Sol No. | $\kappa$. | $p_H$. | $h_p$. | $h_\kappa(P\text{-}V)$. | $h_\kappa(K\text{-}R)$. | $\dfrac{h_\kappa(P\text{-}V)-h_p}{\text{in Per Cent.}}$ | $\dfrac{h_\kappa(K\text{-}R)-h_p}{\text{in Per Cent.}}$ | $h_{t\kappa}$. | $p_{k'}$. | $k$. |
|---|---|---|---|---|---|---|---|---|---|---|
| II | $1\cdot45 \cdot 10^{-4}$ | $3\cdot43$ | $3\cdot71 \cdot 10^{-4}$ | $3\cdot92 \cdot 10^{-4}$ | $3\cdot42 \cdot 10^{-4}$ | $+8\cdot4$ | $-7\cdot8$ | $4\cdot2 \cdot 10^{-4}$ | $3\cdot76$ | $1\cdot74 \cdot 10^{-4}$ |
| III | $2\cdot27 \cdot 10^{-4}$ | $3\cdot24$ | $5\cdot76 \cdot 10^{-4}$ | $6\cdot14 \cdot 10^{-4}$ | $5\cdot35 \cdot 10^{-4}$ | $+6\cdot6$ | $-5\cdot4$ | $7\cdot5 \cdot 10^{-4}$ | $3\cdot64$ | $2\cdot29 \cdot 10^{-4}$ |
| IV | $7\cdot75 \cdot 10^{-6}$ | $3\cdot74$ | $1\cdot82 \cdot 10^{-4}$ | $2\cdot10 \cdot 10^{-4}$ | $1\cdot83 \cdot 10^{-4}$ | $+15\cdot5$ | $+0\cdot5$ | $2\cdot05 \cdot 10^{-4}$ | $4\cdot16$ | $0\cdot69 \cdot 10^{-4}$ |
| V | $3\cdot22 \cdot 10^{-5}$ | $4\cdot04$ | $0\cdot89 \cdot 10^{-4}$ | $0\cdot87 \cdot 10^{-4}$ | $0\cdot76 \cdot 10^{-4}$ | $-2\cdot3$ | $-14\cdot5$ | $1\cdot00 \cdot 10^{-4}$ | $4\cdot40$ | $0\cdot40 \cdot 10^{-4}$ |
| VI | — | $3\cdot24$ | $5\cdot76 \cdot 10^{-4}$ | — | — | — | — | — | $3\cdot64$ | $2\cdot29 \cdot 10^{-4}$ |

Thus by applying the new formula based upon a new conception we get not a worse but a better agreement between conductometric and potentiometric data. The maximum deviation is $-14\cdot6$ per cent., the rest are considerably lower, all $h_k$ being lower than $h_p$. This may serve as an indication that the accepted mobility of the Cl ions is too high; they are to some extent connected with $SiO_2$ particles by adsorption forces which must tend to decrease the mean mobility. The same indication is found in Table I. where the observed conductivity values are lower than those calculated on the assumption that all the $H^+$ and $C^-$ ions of HCl are absolutely free and possess their full mobility.

The values of the electrolytic dissociation constants of colloidal silica found in the paper cited can also be accounted for from the standpoint advanced in the present paper. If we suppose all the acidity of the $SiO_2$ sols to be due to the presence of a strong electrolyte (hydrochloric acid), all our determinations will not meet with the requirement put forward in the paper cited as imperative for the correct determination of dissociation constant of acids from potentiometric titration curves, $viz.$: $p_H$ (of the initial solution) $< p_k$; it cannot evidently hold for strong acids such as hydrochloric acid. It may be noted from Table II. that the values of the dissociation constants found are functions of the initial acidity of the solutions titrated with alkali: for sols III and IV equal values of the constants are found: $p_k = 3\cdot64$. These sols are of equal $p_H = 3\cdot24$. Sol II with a higher value of $p_H = 3\cdot43$ has a lower constant $(p_k = 3\cdot76)$. The same dependence holds for sols IV and V. Thus all previously found values of the constants are " apparent constants " according to the terminology advanced in the paper cited.

The disproportionately small decrease of hydrogen ion concentration observed when diluting silica sols with water noted in that paper, may be probably accounted for by true dissolution of the particles of colloid silica containing hydrochloric acid in a strongly bound form. With increasing dilution and gradual dissolution of particles from the surface, the solubility of colloidal silica containing HCl may grow parallel with the increase of dispersity.

Thus all the experimental data described in that paper may be interpreted from the standpoint advanced in the present paper quantitatively as satisfactorily as from the standpoint of Pauli and Valkó, previously accepted in our laboratory.

### 7. Cation Adsorption on Acid and Alkaline Silica Sols.

The next problem studied in our laboratory was the exchange adsorption of ions on acid and alkaline silica sols. This investigation was made by Z. J. Berestneva.

The adsorption of barium ions was studied. Our purpose being the determination of the amount of adsorbed ions in dependence on the

amount of barium salt added to the sols the problem could not be solved by means of analytical determinations and we resorted to the potentio-metric method. A barium-amalgam flow electrode was constructed, which enabled us to change both the amalgam and the solution to be tested and to make the potential measurements (against a calomel electrode) in an atmosphere of pure hydrogen. This electrode is de-scribed elsewhere.[22] A detailed investigation of its behaviour is given in the same place, showing it to be well adapted for barium ions con-centration measurements, whether in pure solutions of its salts or in mixtures with salts of other metals. The accuracy of the measurements is about $\pm$ 0·5 mV.

Acid silica sols prepared according to Graham and dialysed for ten days (until free from chlorides) were selected. Their $p_H$ varied from 4·7 to 5·17. A comparison between the potentials of $SiO_2$ sols mixed with $BaCl_2$ solutions of the same (initial) concentration showed that under these conditions no barium adsorption on particles of the sols takes place.

On the other hand it was interesting to study the alkaline $SiO_2$ sols, for which we accept the scheme advanced by Pauli and Valkó. They were prepared according to Lottermoser and Kiehn [17] by membrane electrolysis. of a sodium silicate solution. By inter-rupting the electrolysis at fixed time intervals we obtained a series of sols with $p_H$ values ranging from 3·5 to 11·92 and various concentrations. In order to compare the influence of $p_H$ at a con-stant $SiO_2$ concentration they were diluted to make the concentration of each sol equal to 8·39 g./l. The $p_H$ values obtained ranged from 3·5 to 11·38. The results are given in Table III.

TABLE III.

| $p_H$ of Sol. | Amount of $Ba^{++}$ Adsorbed from 0·1 $N$. Solution in g.-equiv./l. |
|---|---|
| 7·90 | 0 |
| 8·79 | 0·0438 |
| 9·85 | 0·0655 |
| 11·38 | 0·0980 |

The comparison of the results of the adsorption measurements in acid and alkaline silica sols leads to the following conception of the character of these sols : The acid $SiO_2$ sols are stabilised by strong acids (chiefly HCl) present in the intermicellar liquid and distributed between it and the particles. Here no adsorption and no ionic exchange takes place. For alkaline sols we accept Pauli's scheme (2) requiring an exchange of ions. Obviously in the transition from the acid sols to the alkaline ones a profound change in the surface structure of the particles takes place, connected with the exchange of ionic groups. We suppose this change to proceed as follows : the gradual addition of alkali to the acid sol first effects the neutralisation of a part of the strong acid, and afterwards the dissolution of the silicic acid with the formation of a corresponding silicate acting as stabilising factor in the alkaline region.

The process of neutralisation of strong acids being stopped with reaching $p_H = 6·5$ to 7, and the perceptible dissolution of silicic acid beginning with $p_H = 8·5$ to 9·5 (Hillebrand) [23] there must exist a $p_H$ range (6·5 to 9·0 approximately) where the particles of colloidal silicic acid are devoid of the stabilising electrolyte and where the stability of the sols is guaranteed solely by the lyophilic properties of the silicic

[22] Z. J. Berestneva and V. A. Kargin, *Acta phys. chim. (Moscow)*, 1, 1934.
[23] W. F. Hillebrand, *Analyse der Silicat-und Carbonatgesteine*, 1910.

acid itself. Obviously a minimum stability must be observed, which was duly found by Ray and Ganguly.[11]

In the same paper by Z. J. Berestneva another important problem bearing on the electrochemistry of colloids was studied, *viz. :* The problem of the *equivalency in exchange adsorption.* In a $SiO_2$ sol ($p_H = 11 \cdot 16$) a barium electrode served for the determination of the $Ba^{++}$ ions adsorption, and a sodium amalgam electrode and a glass electrode for the determination of the amount of ($Na^+$ and $H^+$) cations which were supposed to be removed into the intermicellar liquid in amount equivalent to the amount of $Ba^{++}$ adsorbed. Preliminary experiments showed the readings of the sodium amalgam electrode to be correct in the presence of those low concentrations of $Ba^{++}$ ions (about 0·003 $N$.), which are left in the intermicellar liquid. The $Na^+$ *activity* determinations under these conditions showed that it *remains* practically *constant.* The E.M.F. in volts against a saturated calomel electrode changes from 2·0754 for the pure sol to 2·0711 for a sol with an (initial) $BaCl_2$ concentration of 0·1 $N$. the maximum deviation being: 2·0783 (0·003 $N$. $BaCl_2$), 0·0705 (0·03 $N$. $BaCl_2$). In these concentrations the quantity of Ba ions adsorbed varied from 0·0009 to 0·097 g. equiv./l. It may be supposed that the adsorbed $Ba^{++}$ ions replace not $Na^+$ but the other cation present in the sol, *viz.,* H. Indeed, $p_H$ determinations with the glass electrode corroborate this assumption, but the amount of $H^+$ ions replaced proved quite insufficient for the equivalence with the amount of adsorbed $Ba^{++}$ ions as may be seen from the following Table IV.

TABLE IV.

| $p_H$ of Sol. Initial. | $p_H$ after Adsorption. Final. | Initial Concentration of $Ba^{++}$ in Mixture with Sol (g.-equiv./l.). | $Ba^{++}$ Adsorbed (g.-equiv./l.). | $H^+$ Replaced (g.-equiv./l.). |
|---|---|---|---|---|
| 11·16 | 10·58 | 0·1 | $9 \cdot 7 \cdot 10^{-2}$ | $9 \cdot 13 \cdot 10^{-4}$ |
| 11·16 | 9·56 | 0·2 | $12 \cdot 9 \cdot 10^{-2}$ | $12 \cdot 1 \cdot 10^{-4}$ |

The amount of H ions replaced is approximately one hundred times less than the amount of Ba ions adsorbed.

Thus, it is clear that the equivalence of the cation exchange is not observed in these experiments.

In our other paper [6] this problem was examined more in detail. It has been shown that this assumption can be dispensed with provided we reject the conception of a constant number of charges on the surface of a colloidal particle. It is regrettable that our statement cannot be properly based owing to the scarcity of available experimental data. The present case is one of the few examples of the correctness of this statement.

During the process examined the number of $Ba^{++}$ cations removed from the intermicellar liquid by the particle exceeds the number of ($Na^+ + H^+$) entering it. In order that the electro-neutrality could be maintained it has to be assumed that a certain number of anions, *e.g.,* $Cl^-$ or $SiO_3^{--}$ is adsorbed (entering into the outer component of the double layer) together with the $Ba^{++}$ cations. Preliminary experiments showed a removal of Cl ions from the intermicellar liquid to be actually observed.

## 8. On the Nature of Alkaline Silica Sols.

The alkaline silica sols are interesting not only in relation to the exchange adsorption of ions which they exhibit, but also from the standpoint of their own structure.

The only considerable series of papers devoted to this question emanates from Harman and co-workers.[24] Based upon these investigations and various theoretical considerations Harman treats alkaline silica solutions as systems in true equilibrium, reversible in relation to each component. All properties of such systems are strictly determined by their chemical composition and concentration and do not depend on time or method of preparation.

On the other hand it is known that colloidal systems are not generally regarded as being in true equilibrium and especially for colloidal silica this is not obvious in itself.

S. A. Katz made in our laboratory some experiments bearing on this question. Viscosity measurements of alkaline silica sols having nearly equal chemical composition and concentration but of various degree of ageing proved to be very different as to their viscosity (Table V.).

The age of the sols increases in direction to the higher numbers.

### TABLE V.

| Sol. No. | Mols. $SiO_2$. | Mols. $Na_2O$. | Viscosity in Poise. |
|----------|----------------|----------------|---------------------|
| 1        | 30·0           | 12·5           | 5                   |
| 2        | 30·2           | 12·4           | 70                  |
| 3        | 31·3           | 13·0           | 110                 |

It is seen from this table that the properties of alkaline $SiO_2$ are determined not only by composition and concentration but also by the action of time.

The relation of these sols to the compounds of alkaline earths is important to characterise their properties. It has been investigated by many authors as presenting a great interest also from the technical point of view.

Two main cases of interaction may be considered :

(1) The formation of true chemical compounds (silicates) characterised by the following principal features : stoichiometry in the quantitative ratio of components ; constant vapour or solution pressure of components ; formation of a definite crystal lattice ; (2) The formation of adsorption compounds as result of adsorption of alkaline earths on silicagel ; in this case the requirements of stoichiometry and of the formation of a crystal lattice naturally vanish ; the solution pressure must remain constant according to the above cited standpoint of Harman : all the colloidal properties of the solutions and the adsorption ability of gels connected to the former have to be defined by composition and concentration only.

S. A. Katz and G. Th. Komovsky showed in our laboratory that in the interaction of sodium silicates of various composition with calcium chloride solutions gels are obtained giving X-ray photographs by Debye-Scherrer's method having only one diffused maximum (responding to the 111-plane of cristobalite). The same maximum was obtained for these

[24] R. W. Harman, *J. Physic. Chem.*, **29,** 1155, 1925 ; **30,** 359, 917, 1100, 1926 ; **31,** 355, 616, 1927 ; **32,** 44, 1928.

precipitates after complete removal of CaO by treating them with 0·1 N. hydrochloric acid. We can suppose that this maximum is due to the recrystallisation of $SiO_2$ gel to cristobalite. No other maxima have been observed. Such new maxima have been found only on heating the gel above 800° C. Below this temperature the above-mentioned picture holds.

The $SiO_2$, CaO precipitates being amorphous, great interest must be attributed to the study of their solution pressure, as it is the only remaining means of verifying Harman's assumption, by seeing whether it depends only upon chemical composition and concentration or can be influenced equally by other factors. In the last case we should have to recognise these systems as irreversible systems.

S. A. Katz showed that in titrating silicates (of similar chemical composition but differing in age and viscosity), by $CaCl_2$ solutions, and following the change of $p_H$ values by means of a glass electrode we obtain curves of different form. This points to the variability of solution pressure, the $p_H$ value being dependent on the concentration of $Ca^{++}$ ions in the solution. In Fig. 3 $p_H$ values are plotted against the added amount of $CaCl_2$ solution in c.c.; the results are given for metasilicate ($Na_2SiO_3$) of various age: freshly prepared (curve 1), 2 days old (curve 2), 7 days old (curve 3). The only apparent difference between the sols lies in their varying viscosity which points to differences in internal structure. Sol No. 2 has a viscosity of 120, No. 3—of 30, No. 5—of 0·9 poise.
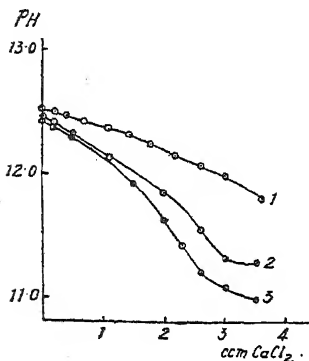


FIG. 3.

Thus, solution pressure, X-ray methods, change of viscosity with time induce us to think that true chemical compounds are not formed in these cases and that the colloidal properties of alkaline $SiO_2$ solutions are not defined merely by their composition and concentration.

## Summary.

1. A general survey of problems connected with the electrochemical properties of colloidal silica is given. Contradictions in the views on the structure and properties of these systems have been pointed out.

2. The part of the investigation carried out by A. J. Bybaev is devoted to the study of extremely pure silica sols obtained by hydrolysis of silicon tetrachloride, purified by dialysis and a prolonged electrodialysis at a high potential fall.

3. No difference is observed between the conductivity of such sols and the conductivity of twice-distilled water, i.e., their compensating ions (Gegenionen) do not perceptibly increase the conductivity of water. Gels obtained from these sols are readily peptised by hydrochloric acid.

4. Furthermore very pure $SiO_2$ sols were obtained by a new method— by oxidation of silane ($SiH_4$) by ozone in water. These sols also have no acid properties, showing $p_H$ values approximating 7.

5. It is demonstrated that *pure* silica sols are neutral and have a very small concentration of compensating ions, which cannot be measured by any existing electrometric method.

Their stability is apparently due to lyophilic properties of silicic acid.

6. Determinations carried out by A. J. Bybaev on highly acid (slightly dialysed) $SiO_2$ sols showed their H-ion-concentration to be equivalent to the Cl ion concentration and therefore all the electrometrically found ions belong to the HCl of the intermicellar liquid.

7. Cataphoretic experiments carried out by A. J. Bybaev showed the potential of acid $SiO_2$ sols to be very small and frequently equal to zero. This corroborates the above conclusion as to the small amount of compensating ions accounting for the absence of exchange adsorption on acid $SiO_2$ sols.

8. The high acidity of silica sols studied by other authors is accounted for by their insufficient purification from hydrochloric acid in the process of electrodialysis. The experimental data of the paper by Rabinovitch and Laskin, particularly the high values of the dissociation constants of colloidal silica are accounted for from the same standpoint.

9. In the part carried out by Z. J. Berestneva the absence of cation adsorption in the coagulation of acid silica sols by electrolytes is proved.

10. In the study of the coagulation of alkaline $SiO_2$ sols the $Ba^{++}$ ions were found to be absorbed by the colloidal particles, but no equivalent exchange adsorption was observed : the amount of cations replaced being far less than that of the cations adsorbed.

11. The study of interaction between silica and salts of metals of alkaline earths carried out by S. A. Katz and G. Th. Komovsky showed that no true chemical compounds are formed but only adsorption compounds. The solution pressure of CaO in these compounds depends on the age of the precipitate.

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# POLYMERISATION PHENOMENA OF SILICIC ACID.

## By W. D. Treadwell (*Zürich*).

The potentiometric titration of sodium metasilicate with hydrochloric acid shows a flat potential drop at $p_H = 10 \cdot 9$ and a subsequent very sharp one with its steepest part near $p_H = 6 \cdot 8$. Taking the half-neutralisation points on the curve as the values of the dissociation constants of monosilicic acid we get :[1]

$$K_1 = 10^{-9,7} ; \quad K_2 = 10^{-12}$$

Similar values have already been given by various authors. Hägg[2] gives the following data : $K_1 = 10^{-9}$; $K_2 = 10^{-13}$. Britton's[3] values are $K_1 \sim 10^{-9 \cdot 5}$; $K_2 \sim 10^{-11 \cdot 7}$. With other authors Britton draws attention to the fact that the ionisation of silicic acid cannot be represented satisfactorily in terms of two dissociation constants. The low value of $K_1$ is not in agreement with the second sharp potential drop in the titration curve. It has been generally accepted, that this deviation is caused by a considerable polymerisation of the primarily liberated monosilicic acid.

[1] *Helv. Chim. Act.*, **13**, 842, 1930.    [2] *Z. anorg. Chem.*, **155**, 21, 1926
[3] *J. Chem. Soc.*, **129**, 425, 1927.

It can easily be seen that the acidimetric titration of alkali silicate is directly reversible on the alkaline side.   In back-titrations from the acid side the attainment of equilibrium appears to be very notably retarded in the neighbourhood of the neutral point.   This must be due to the slowly advancing peptisation of polymerised silicic acid by the added alkali, a reaction which has to precede the formation of the stable disilicate ions.

The difference between the two dissociation constants of silicic acid, given as $\Delta p_K = 2\cdot3$ is considerably smaller than the corresponding value for carbonic acid, $i.e.$, $\Delta p_K = 4\cdot67$, which seems to indicate that the acid groups in silicic acid are considerably farther apart.   This might be explained by the statement of N. V. Sidgwick [4] that silicon, contrary to carbon is able to expand its octet.   Doing this by hydration, the greater distance of the acid groups in silicic acid and furthermore a certain tendency for the formation of chains with oxygen bridges in the process of polymerisation could be understood.

The above described titration curve of sodium metasilicate changes totally when 50 per cent. alcohol is added to the aqueous solution.   The disilicate step disappears in this case and the altered curve now very much resembles the neutralisation curve of a strong alkali.[1]

Silicic acid sols are generally prepared by using Graham's method of pouring a solution of sodium silicate into an excess of dilute hydrochloric acid, the sodium chloride formed and the excess of acid being removed as far as possible by dialysis.[5]   Such sols have a strong tendency to gelatinise.

When the last traces of sodium are removed by electrodialysis the sols become more stable and their acidity reaches the remarkably high values of $p_H = 3\cdot2$ to $3\cdot6$.   Silicic acid sols of such an acidity have been investigated by Pauli and Valko [6] and by Rabinowich and Laskin.[7] Lottermoser and Kiehn have recently prepared acid sols from alkali silicate by membrane electrolysis and subsequent electro-dialysis.

Pauli and Valko explain the high acidity of these sols by assuming the formation of an acid with a colloidal anion,

$$(SiO_2)_x \cdot nH_2O \cdot ySiO_3H' + yH^{\cdot},$$
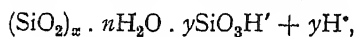
of which the anion reacts easily with hydroxyl ion according to :

$$(SiO_2)_x \cdot nH_2O \cdot ySiO_3H' + OH' \rightarrow (SiO_2)_{x-1} \cdot nH_2O \cdot ySiO_3H' + SiO_3H'.$$
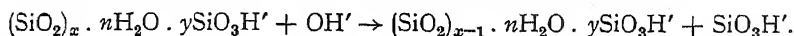
This opinion has been endorsed by the studies of Rabinowich and Laskin on the neutralisation and buffering power of these sols.

It seemed interesting to ascertain whether pure silicic acid could be prepared by removing the metal from alkali silicate by electrolysis with a mercury cathode.   The discharge of the silicate anions on the platinum electrode leads to evolution of oxygen and the formation of silicic acid.

To get a rapid extraction of the alkali, the mercury was circulated through the electrolysing cell by a centrifugal pump.   The latter consisted of a rotating glass tube, placed vertically in a mercury container, which communicated with the electrolysing cell.   As outlets for the mercury two small holes were bored through the pump shaft, just above the level of the metal.   The mercury was emulsified in the supernating liquid, which consisted of an aqueous solution of carbon dioxide.   This solution

[4] " The Electronic Theory of Valency."    [5] $Phil. Trans.$, 151, 183, 1861.
[6] $Koll. Z.$, 36, 334, 1925.                    [7] $Z. physikal. Chem.$, 134, 387, 1928.

which was continuously replaced, had to decompose the liquid amalgam. To facilitate this reaction as much as possible a cylinder of platinum foil was dipped into the mercury in such a way, that the droplets of the metal after having passed through the carbonic acid solution, were hit against the platinum foil. Fig. 1 shows the construction of the apparatus. The centrifugal pump is seen to the left of the electrolysing cell, on the right side of the figure. In the circulation system of the mercury three traps for catching moisture and hydrogen bubbles are inserted.

Within five hours 150 c.c. of 0·5 $M$ $Na_2SiO_3$ could be transformed into pure acid, beginning with a current of 2·8 amp. and a voltage of 4·3. At first the $p_H$ amounted to 12·45. Within 120 minutes the disilicate step was reached ; 180 minutes later the second large potential drop appeared in the $p_H$-curve and 60 minutes later the $p_H$ had come to its constant value of 3·2.
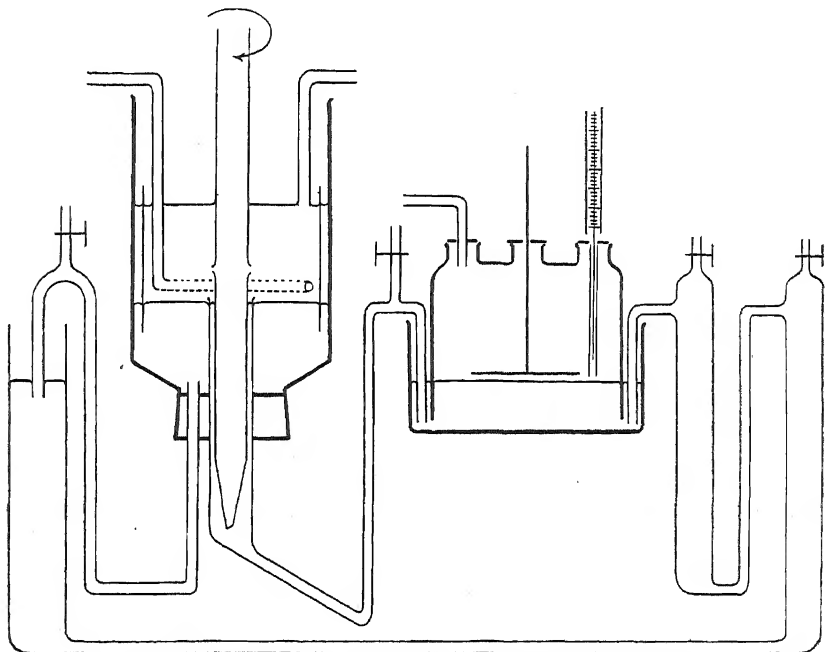


FIG. 1.—Electrolytic cell for the preparation of silicic acid.

The extraction of the alkali could be done more quickly if desired. The method proved to be convenient for the preparation of silicic acid sols of given concentration.

The $p_H$ curve of the solution during the course of the electrolysis was practically that of an acidimetric titration of sodium silicate, which shows that the liberated acid remains in a sufficiently active form to establish equilibrium with the remaining alkali.

Electrolysis of a 0·1 $M$ $Na_2SiO_3$ solution led to a specimen of silicic acid of $p_H = 5·4$. After remaining in a closed vessel for five days the acidity of the solution had increased to $p_H = 3·4$, showing that a slowly advancing partial polymerisation of the silicic acid had to precede the formation of the acidosol.

The work of Willstätter, Kraut and Lobinger [8] indicates the polymerisation of mono- and disilicic acids. In the course of these reactions

[8] Ber., 61, 2280, 1928 ; 62, 2027, 1929.

we may assume, also, a rapid condensation between disilicate ion and polysilicic acid, as these particles, having a sufficient mobility, will be able to approach each other without having to overcome a considerable potential barrier.

The condensation of basic aluminium chlorides with hydrates of alumina seems evidently to be similar to the above-mentioned reaction. The polymer hydrates which are very readily formed in this way show properties distinctly different from those of ordinary aluminium hydroxide.[9]

## Determination of the Molecular Weight.

For a reliable measurement of the lowering of the freezing-point of partly colloidal solutions it has been found necessary to modify the ordinary Beckmann method in the following way :

In a double walled test-tube about 25-50 c.c. of solution was cooled exactly to zero, whereupon 1-2 gr. of finely powdered ice (produced by freezing a current of steam at − 80°) equally brought to the temperature of zero, was thrown into the solution. Operating with 0·1 $N$ or 0·01 $N$ NaCl the temperature equilibrium was established, upon stirring, within one minute. While blank tests gave no change of temperature, the depression of 0·001 $N$ NaCl could still be measured.

TABLE I.

| Age of Sol in Hours. | Viscosity $\eta_t$. | Constant $a$ in $\eta_t = \eta_0/(1 - at)$. |
|---|---|---|
| 0 | 2 | |
| 110·00 | 2 | |
| 10 | 2·45 | 0·01837 |
| 20 | 3·2 | 0·01875 |
| 30 | 4·7 | 0·01870 |
| 40 | 8·5 | 0·01916 |
| 45 | 14·5 | 0·01916 |
| 47 | 21·0 | 0·01925 |
| 50 | 51·0 | 0·01922 |
| 51 | 115·0 | 0·01927 |
| 52 | 342·0 | 0·01912 |
| 53 | 605·0 | 0·01882 |
| 54 | 1144·0 | 0·01850 |
| 55 | 1683·0 | 0·01816 |

Our silicic acid solutions behaved differently from sodium chloride, in so far as they required considerably more time for the establishment of temperature equilibrium, the time necessary increasing steadily with the age, *i.e.*, the polymerisation, of the silicic acid. This phenomenon indicates the colloidal nature of the solution.

The observed retardation may be taken as a measure of the reduced mobility of the molecules of silicic acid within the existing colloidal particles. If the polymerisation were limited to the formation of single chains of polysilicic acid, the observed retardation of temperature equilibrium would not be comprehensible. It seems therefore that long chains of polysilicic acid, according to Staudinger's opinion, must be very unstable, owing to their tendency to form an irregular network of loosely coherent secondary particles of a more or less spheric shape. This view seems to be also supported by the fact that double refraction has not yet been observed with flowing particles of colloidal silicic acid.

In freshly prepared solutions of 0·5 empirical molar $H_2SiO_3$ an average molecular weight of 149·4 was found, which increased at a rate of 22·2 per hour. Beyond 1015, the molecular weight increased more slowly, reaching the value of 1240 after 86 hours.

By titrating a 0·5 $M$ acid sol of $p_H = 3·2$ with alkali to $p_H = 5$, the following ratio was obtained : $SiO_2 : H^· = 600$.

V. R. Main [10] has found that the viscosity of alkali silicate solutions

[9] *Helv. Chim. Act.*, 14, 473, 1931 ; 15, 980, 1932.
[10] *J. Physic. Chem.*, 30, 535, 1926.

begins to increase more rapidly on the upperside of the disilicate step, *i.e.*, when the solution contains more than 2 mols. of silicic acid per mol. of alkali, the excessive acid showing a decided tendency to form a sol.

This seems to explain also our observations on the reaction of egg albumin with solutions of sodium silicate. We observed a turbidity with egg albumin in our electrolised $0.5$ $M$ silicate solutions downward from $p_H = 10.2$, the acidity of the disilicate step being $p_H = 10.9$. The starting-point of the albumin precipitation corresponded to a ratio of

$$SiO_2 : NaOH = 1.2.$$

At this acidity, alkali silicate is represented by a somewhat complicated system of disilicate ions, free acid and sol particles of different rates of polymerisation. The further alteration of the sol can easily be observed by viscosity measurements.

### Viscosity Measurements.

The viscosity of sol particles consisting of very loosely coherent aggregates, as is the case with silicic acid sols, should be measured with an apparatus of low velocity gradient. The apparatus, which we used was one of the Couette type with a velocity gradient of $0.2$. The solution was placed in a beaker, rotating fifteen times per hour. In the axis of the beaker a test-tube with a narrow neck was suspended on a galvanometer wire, the length of which could be varied roughly between 40 and 60 cm. The solution was filled up to the neck of the test-tube. The torsion of the wire could be measured and gave empirical values of the viscosity. The regions of small deflections have been calibrated by measurements with cane sugar.
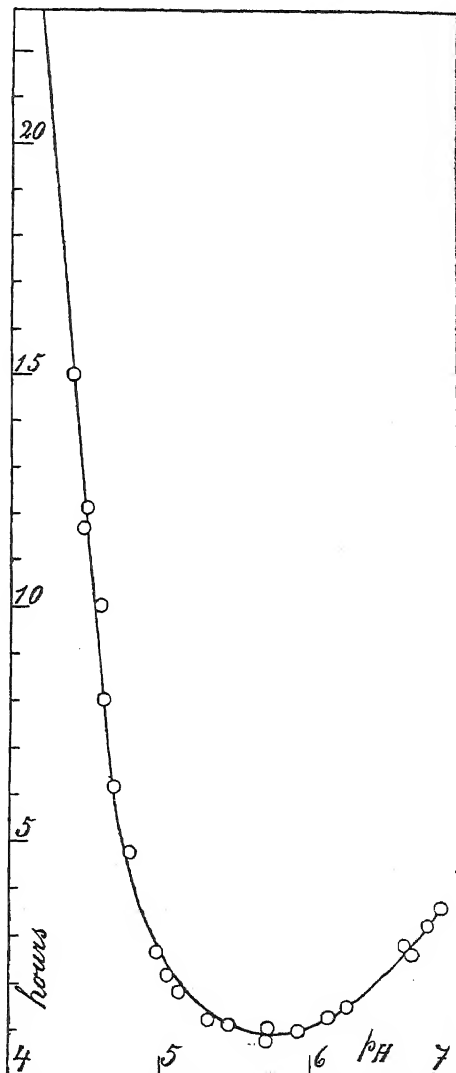


FIG. 2.—Time — $p_H$ — curve of the gelatination of $0.5$ m. silicic acid.

Table I. shows the behaviour of a salt-free solution of $0.5$ $M$ silicic acid of $p_H = 3.2$. After standing 110 hours the solution showed a

viscosity only a few per cent. higher than water, while the molecular weight had been increasing from 159 to 1500. Hereafter the viscosity became four times as large within forty minutes, and ten minutes later the solution had become a solid gel.

From the beginning of the rapid gelatination the increase of the viscosity seems to be essentially due to the growing inclusion of solute by the growing particles. If we assume this process to be proportional to time, the viscosity $\eta_t$ at the time $t$ may be represented by :

$$\eta_t = \frac{\eta_0}{1 - at}$$

where $\eta_0$ denotes the viscosity at the beginning of the period of rapid gelatination. As will be seen from Table I. the factor $a$ appears to be fairly constant.

Within the range of $p_H = 3$ to 9·8 the acidity of the 0·5 $M$ sols showed a tendency to decrease slowly. In the course of 260 days the $p_H$ changed at a rate proportional to the initial acidity, $p_{Hi}$, the alteration amounting to :

$$\Delta p_H = (9·8 - p_{Hi})\ 0·167.$$

The greater part of this alteration was observed in the state of the solid sol.

Syneresis appeared most abundantly in the highly purified gels and decreased rapidly with rising $p_H$-values, in agreement with the observations of D. G. R. Bonnell.[11]

At the moment of gelatination neither an evolution of heat nor a break in the conductivity curve could be observed.

The time required for gelatination of the 0·5 $M$ sols as a function of their acidity is represented in Fig. 2. The shortest time required for gelatination was observed at $p_H = 5·8$, i.e., at an acidity where the hydrogen ions of the acidosol were practically neutralised.[12]

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## GENERAL DISCUSSION.*

**Dr. E. Valkó** (*Ludwigshafen a/Rh.*) said : In the discussion of the paper of Rabinovitch and Kargin, I have already pointed out that their criticism of our determination of the activity of the *Gegenions* is not well founded. If the single electric charges at the surface of colloid particles are at a sufficient distance apart, the double layer is diffuse enough to result in a practically complete freedom for *Gegenions*. It is very probable that the silicic acid sols are such systems. In this case one finds the activity of *Gegenions* corresponding to the whole charge of the colloid ion.

Our assumption, that in the electrodialytic purified sols all charging ions are attached to the colloid, made in our paper in 1925, was based on the following points :—

(1) The dialysis leads to a minimum limit of sol conductivity, which remains constant even if the dialysis is continued for several weeks.

[11] *Trans. Faraday Soc.*, **28**, 1, 1932.     [12] *Helv. Chim. Act.*, **16**, 473, 1933.
    * On two preceding papers.

(2) Electrodialysis with a potential gradient of about 2 volts/cm. leads often to an increased conductivity in consequence of the exchange of sodium ions against H-ions. The equivalent concentration of sol remains essentially unchanged. Impurities, however, must be driven out in a much shorter time than the duration of the electrodialysis.

(3) Electrodecantation, the mechanism of which is the forming of a layer of the concentrated sol as a consequence of electrophoresis, leads to the following situation : the lower layer consists of the sol with a correspondingly high conductivity and H-activity, the upper layer does not consist of silicic acid, and has the conductivity of pure water.

(4) In a parchment membrane the sol shows an osmotic pressure approximately corresponding to the activity of the *Gegenions.*

On the basis of these facts it is impossible to suppose that a large part of the charging ions is free.

On the other hand, we have already observed the influence of the HCl in the production of sol for its electrical properties. The Graham sols, prepared in the presence of much HCl had an equivalent charge about ten times as large as that of the Grimaux sols, prepared by the hydrolysis of silicic methyl ester in pure water. Certain Grimaux sols, the properties of which we have described had a conductivity of only $10^{-6}$ with a content of 1 per cent. to 2 per cent. $SiO_2$. The sols of Rabinovitch and Kargin contain only 0·02 per cent. $SiO_2$. If we diluted our sol to 0·02 per cent. we should have, like Kargin and Rabinovitch, a conductivity, which is not markedly different from the conductivity of pure water. It is evident, that for investigations into the electro-chemistry of colloids with huge equivalent weights, only concentrated solutions are suitable.

Furthermore, we found, that the hydrolysis of silicic methyl ester in 1 $N$ HCl results in sols with similar properties to the Grimaux sols. On the other hand, the hydrolysis in 0·1 $N$ NaOH and purification after gives also sols with a lower but marked activity. It is difficult to think that in the latter case the presence of a foreign acid should be the cause of the activity. We prefer to assume that the effect of HCl is due to its influence on the process of polymerisation (condensation and hydration) of silicic acid in favouring the formation of a comparatively well-ionised and stable kind of silicic acid molecule at the surface of the colloid particles.

We have also the impression, that the facts found by Treadwell and co-workers in their valuable investigation as to the electrolytic preparation of silicic acid rather support our interpretation.

**Professor A. J. Rabinovitch,** in reply, said : The disagreement on the determination of the activity of the *Gegenions* still remains unsettled. No considerations of the detailed mechanism of electrolytic dissociation can settle the basic discrepancy between the activities measured by the potentiometric and the osmotic methods in colloidal systems, which is an offence to the second law of thermodynamics. The only solution of this problem available at the present time seems to be that given in our first paper.

As to the second point of Dr. Valkó's criticism, we regret that no experiments with electrodialysis in more severe conditions have been made in Vienna. This would show whether the states reached correspond really to equilibrium conditions.

Thirdly, Dr. Valkó mentions some observations on Grimaux-sols of silicic acid. Unfortunately the silicic acid esters are obtained from

preparations containing chlorine, and therefore the sols cannot be com-
pletely freed from HCl and other chlorine containing compounds.

**Dr. F. Eirich** (*Wien*) said : Measurements have recently been made
in Pauli's Institute of the conductivity, $p_H$ and alkaline titre of Graham's
silicic acid sols. Our potentiometrical and conductometrical curves
of titrations were of the same shape as the curves Professor Treadwell
got in the case of metasilicic acid. But even Professor Rabinovitch
in the paper with Laskin found the same course of H and $p_H$. Unfor-
tunately he stopped his titrations too early, *i.e.* whilst the shape of
the curves shows that the titration is not yet finished. I believe that
it would be too remarkable if this extraordinary agreement between the
behaviour of metasilicic acid and colloidal silicic acid were not of some
importance.

Generally, one cannot too much emphasise that sols prepared in a
different manner are frequently of different types and may have quite
different behaviour. They all have their individual details and one of
the greatest difficulties in colloid chemistry is to find out general qualities
even in electrochemical behaviour which are nevertheless comparatively
well-defined. We are, therefore, in agreement with Professor Treadwell,
grateful to Professor Rabinovitch for describing to us a new interesting
type of preparation of silicic acid sol ; we cannot, however, agree that
in consequence he is entitled to draw such important conclusions in
respect to the general nature of colloidal silicic acid.

**Professor A. J. Rabinovitch,** in reply, said : As shown in Fig. 3
of the paper by Rabinovitch and Laskin, some of our titrations were con-
ducted far enough and still did not show the second inflection point found
by Eirich. If this point really exists it may be attributed to the silicic acid
itself (corresponding to its *first* dissociation constant) ; the first inflexion
point on the potentiometric curve and the corresponding conductivity
minimum can be ascribed to a strong acid, *e.g.* HCl.

With regard to the statement of Dr. Eirich that various $SiO_2$-sols
possess different properties, we consider this fact as an argument against
the validity of the general scheme of structure of these sols given by
Pauli and Valkó (see Equation 1 of our papers).

**Professor E. Elöd** (*Karlsruhe*) said, with regard to Professor
Treadwell's paper : I may point out an interesting analogy. If to an
aqueous solution of a chromium salt, *e.g.* of $CrCl_3$ a certain quantity
of $N/10$ sodium hydroxide is added, the $p_H$ value of the solution gradually
rises until it reaches the point of neutralisation. On back titration with
a $N/10$ solution of hydrochloric acid, the corresponding $p_H$ previous
values will never be attained by adding equivalent amounts of sodium
hydroxide. Rather, the $p_H$ value rapidly drops into the acidic region
by already adding smaller amounts of hydrochloric acid and only then
slowly reaches the initial value. This shows that, at the aforesaid
point of neutralisation or near it, polymerisation phenomena cause
partial mutual saturation among a part of the valencies of the chromium
hydroxide particles which have arisen by the addition of sodium hydroxide.
These bound valencies are then removed from the subsequent action
of hydrochloric acid. (Cf. Bjerrum, *Zs. physik. Chem.*, **73**, 727, 1910.)

# PART II. (D) PROTEINS.

# THE REACTION BETWEEN PROTEIN FIBRES AND SUBSTANTIVE DYESTUFFS.

## (XXII. COMMUNICATION CONCERNING MORDANTING AND DYEING PROCESSES.) [1]

By E. Elöd (*Technische Hochschule Karlsruhe*).

.(From experiments by N. Balla.)

In the works of E. Elöd and his co-workers the reactions involved in the dyeing of wool, silk and hides (*e.g.*, chrome leather) with acid dyestuffs were explained.[2] The results of these researches showed that the mechanism of the taking up of acid dyestuffs from acid solutions was as follows : in the first place a protein salt of this acid is formed due to the great diffusibility of the colourless acid. With the appearance of the protein salt the membrane action of the fibre comes into play ; this then causes an unequal distribution of the dyestuff anions between fibre and dyebath according to the equation

$$\frac{\text{Dyestuff anion in the fibre}}{\text{Dyestuff anion in the dye-bath}} = 1 + \frac{C_1}{C_2 + C_3} = \lambda.*$$

According to this conception there is a time lag between the formation of the protein salt and the taking up of the dyestuff. These two separate reactions can in fact be transiently separated from each other.[3] It has further been ascertained that the taking up of dyestuff passes through a maximum ; a characteristic which we can explain by our theory as to the taking up of dyestuffs, developed along the lines of the Donnan theory of membrane equilibrium.

We have further shown that the chlorine ions from the protein chlorides first formed, as stated above, are displaced by the acid-dyestuff anions during the dyeing process. Thereby further proof is afforded that there is a chemical combination between dye acid and fibre protein.

In connection with this work it was interesting to investigate the reaction of the substantive dyes towards wool, silk and hides. The substantive dyestuffs are chiefly sodium salts of sulpho acids ; their particles in aqueous solution are substantially larger than those of acid dyestuffs. It was normally to be expected that these dyestuffs would react, with respect to their acid character, in the same way as acid dyestuffs. That is to say, in this case also the taking up of dyestuff should follow the rules established by E. Elöd and his co-workers. On the other hand, it was also to be expected that the substantive dyestuffs, in their action

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[1] XXI. Communication, see this vol., p. 216.
[2] E. Elöd, *Trans. Faraday Soc.*, **29**, 327, 1933 ; E. Elöd and F. Böhme, *Mell. Textilber.*, 365, 1932 ; E. Elöd and A. Köhnlein, *Collegium*, 1933, 754.
[3] E. Elöd, *i.e.*, *Trans. Faraday Soc.*, **29**, 327, 1933.
* Where $C_1$ = hydrogen ion concentration in the fibre. $C_2$ = hydrogen ion concentration in the dye-bath. $C_3$ = dyestuff concentration in the bath.

on the protein fibres, would show those characteristics which are consistent with their colloidal character, and which accordingly differ from those found in acid dyestuffs. In order to explain the relations between them we will briefly summarise the present-day conception as to the substantive dyeing of cotton. According to this, the substantive dyeing is brought about by exchange reaction between the secondary valencies arising from the hydroxyl groups of the cellulose and the corresponding secondary valencies of the substantive dyestuffs. It is probable that this kind of dyeing can only take place when the dyestuff has a long chain structure, which attaches itself to the elongated cellulose chain. Whether in this reaction the colloidal character of the substantive dyestuff plays the decisive rôle, in contradistinction to that of the molecular dispersion of the acid dyestuff, must still be left undecided.

## Experiments with unloaded Natural Silk.

Natural silk is easily dyed with substantive dyestuff in either the loaded or unloaded condition. Natural silk also, as is well known, shows, just like cotton, a decided " fibre-structure " ; in other words, from the results shown by the Röntgen diagram, their crystallites are oriented parallel with the fibre axis. It follows that the elongated dyestuff particles of the substantive dyestuffs orientate themselves, according to the secondary valencies along the crystallites of the silk. It is, on the other hand, certainly possible that the substantive dyestuffs react in acid solution with the silk proteins, i.e., with their amino groups, in the same way as the acid dyestuffs.

The following work seeks to explain whether the first or the second reaction predominates or whether both occur simultaneously.

It has been found that with increasing hydrogen ion concentration in the dye-bath ($p_H = 5$ to $1$), the taking up of substantive dyestuff by silk increases steadily. This result conflicts with our observations on the action of acid dyestuffs on silk ; in the former case, no maximum for taking up of dyestuffs with increasing hydrogen ion concentration was found. Probably the dyestuff is flocculated in strongly acid conditions and is then taken up, either on the surface of or inside the fibre, owing to preponderating adsorption combinations. This leads to an increased absorption of dyestuff, whereby the expected maximum is masked. Within these ranges of hydrogen ion concentration, both reactions (i.e., the chemical and the adsorptive), consequently comes into play. How the relations stand in weaker acid ranges (i.e., whether a purely chemical taking up of the dyestuff preponderates or whether also the colloidal properties of the dyestuffs already appear), cannot as yet be clearly explained. It would undoubtedly be preferable to seek a statistical relationship. Such calculations are however uncertain, for in the case of substantive dyestuffs, by reason of their larger particles, there is a substantially lower diffusion velocity and thereby a slower attainment of the end point of the dyeing. On the other hand it is not easy to discover whether, when the experiments last too long, the protein fibres themselves exert an undesirable influence due to proteolysis

*Unloaded* silk was dyed with varying quantities of dialysed diamine-sky-blue F.F. (calculated on the weight of silk at 50° C.) and 80° C. The experimental time was generally one hour ; the dye-bath ratio 1 : 30 and 1 : 50. The dyeing experiments were carried out with and without additions of sodium sulphate (Table I.). The higher temperature (80° C.) was chosen for the reasons mentioned later, in connection with the work on wool. The reproducibility of the measurements was good. In the last column there is shown the quantity of dyestuff recovered after dyeing and centrifuging the dyed silk hanks, when the silk was placed in colourless solutions whose $p_H$ value was so adjusted that they corresponded to the

$p_H$ values of the dye baths after dyeing had taken place.  (" $p_H$ after dyeing," in the tables).

In most of the experiments an increasing $p_H$ value showed that an increasing amount of dyestuff was returning into solutions.

The taking up of dyestuff was measured colorimetrically by means of a Pulfrich " Stufen-photometer " of Zeiss.

TABLE I.

| Experiment No. | $p_H$ Before Dyeing. | After | Dyestuff Absorption in mg. per 1 grm. Silk. | Dyestuff Liberated in mg. per 1 grm. Silk. |
|---|---|---|---|---|

5 per cent. diamine-sky-blue FF calculated on the weight of silk.  Bath ratio 1 : 50.  Temperature, 50° C.

| | | | | |
|---|---|---|---|---|
| 1 | 0·50 | 0·52 | 33·00 | traces |
| 2 | 1·10 | 1·10 | 30·50 | ,, |
| 3 | 1·48 | 1·50 | 27·60 | 1·00 |
| 4 | 1·95 | 2·07 | 27·60 | 1·80 |
| 5 | 3·00 | 3·65 | 25·60 | 3·00 |
| 6 | 3·80 | 4·65 | 18·00 | 4·40 |
| 7 | 4·90 | 5·00 | 16·60 | 4·40 |
| 8 | 5·95 | 5·58 | 16·00 | 4·20 |

5 per cent. diamine-sky-blue FF + 15 per cent. $Na_2SO_4$ calculated on the weight of silk.  Bath ratio, 1 : 50.  Temperature, 50° C.

| | | | | |
|---|---|---|---|---|
| 1 | 0·70 | 0·70 | 31·20 | traces |
| 2 | 1·00 | 1·10 | 30·00 | ,, |
| 3 | 1·40 | 1·40 | 30·00 | 0·30 |
| 4 | 2·15 | 2·27 | 23·60 | 0·80 |
| 5 | 2·90 | 4·05 | 19·20 | 0·80 |
| 6 | 4·05 | 4·50 | 11·20 | 1·20 |
| 7 | 5·50 | 5·37 | 10·00 | 1·80 |
| 8 | 6·25 | 5·95 | 4·20 | 2·00 |

5 per cent. diamine-sky-blue FF calculated on the weight of silk.  Bath ratio, 1 : 50.  Temperature, 80° C.

| | | | | |
|---|---|---|---|---|
| 1 | 0·47 | 0·68 | totally extracted | none |
| 2 | 0·90 | 1·10 | ,, | ,, |
| 3 | 1·20 | 1·40 | ,, | ,, |
| 4 | 1·90 | 2·12 | 48·00 | traces |
| 5 | 2·82 | 4·10 | 44·80 | 1·3 |
| 6 | 3·85 | 4·97 | 36·00 | 2·5 |
| 7 | 5·45 | 5·33 | 34·00 | 3·0 |
| 8 | 5·80 | 5·70 | 31·80 | 3·5 |

5 per cent. diamine-sky-blue FF + 15 per cent. $Na_2SO_4$ calculated on the weight of silk.  Bath ratio, 1 : 50.  Temperature, 80° C.

| | | | | |
|---|---|---|---|---|
| 1 | 0·47 | 0·70 | totally extracted | none |
| 2 | 0·90 | 1·10 | ,, | ,, |
| 3 | 1·20 | 1·42 | ,, | ,, |
| 4 | 1·90 | 2·33 | 47·00 | traces |
| 5 | 2·82 | 4·03 | 39·20 | 1·30 |
| 6 | 3·85 | 5·57 | 24·00 | 2·50 |
| 7 | 5·45 | 5·35 | 22·00 | 3·00 |
| 8 | 5·85 | 5·60 | 21·00 | 3·50 |

In order to discover whether there was any difference in the effect of using dialysed or undialysed dyestuffs, experiments were carried out with undialysed dyestuffs (Table II.).

TABLE II.

| Experiment No. | $p_H$ | | | Dyestuff Absorption in mg. per 1 grm. Silk. | Dyestuff Liberated in mg. per 1 grm. Silk. |
|---|---|---|---|---|---|
| | Before Dyeing. | | After | | |
| 5 per cent. diamine-sky-blue FF calculated on the weight of silk. Temperature 50° C. | | | | | |
| 1 | 0·80 | | 1·10 | 45·00 | none |
| 2 | 1·00 | | 1·10 | 41·00 | traces |
| 3 | 1·25 | | 1·27 | 35·00 | ,, |
| 4 | 1·95 | | 2·02 | 29·50 | 0·75 |
| 5 | 2·70 | | 3·57 | 27·00 | 1·00 |
| 6 | 4·05 | | 4·92 | 12·10 | 2·00 |
| 7 | 5·25 | | 5·45 | 7·20 | 2·00 |
| 5 per cent. diamine-sky-blue FF calculated on the weight of silk. Temperature 80° C. | | | | | |
| 1 | 0·80 | | 1·01 | totally extracted | none |
| 2 | 1·00 | | 1·01 | ,, | ,, |
| 3 | 1·25 | | 1·37 | ,, | ,, |
| 4 | 1·95 | | 2·02 | ,, | ,, |
| 5 | 2·70 | | 3·65 | 45·20 | traces |
| 6 | 4·05 | | 4·95 | 20·80 | 1·00 |
| 7 | 5·20 | | 5·45 | 16·50 | 1·00 |
| 8 | 6·25 | | 6·25 | 5·00 | traces |
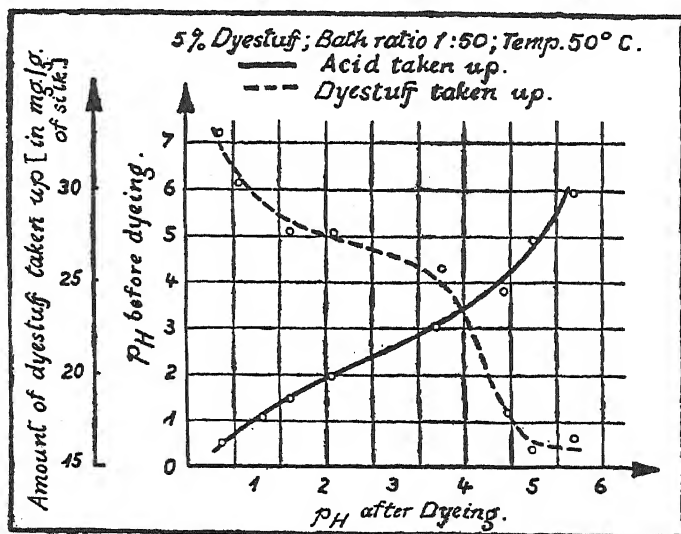


FIG. 1.—Amount of acid and dyestuff taken up by unloaded silk.

From the Tables I. and II. (Figs. 1 and 2) one sees that silk reacts differently towards substantive dyestuffs than towards acid dyestuffs. It should be recognised that there is a connection between the taking up of dyestuff and the hydrogen ion concentration of the solutions, but there

is no maximum of dyestuff absorption. As was suggested in the first instance, it is possible that the substantive dyestuffs are fixed not only chemically but also by adsorption and that then the absorption of dyestuff masks the reaction which ought to take place according to the Donnan
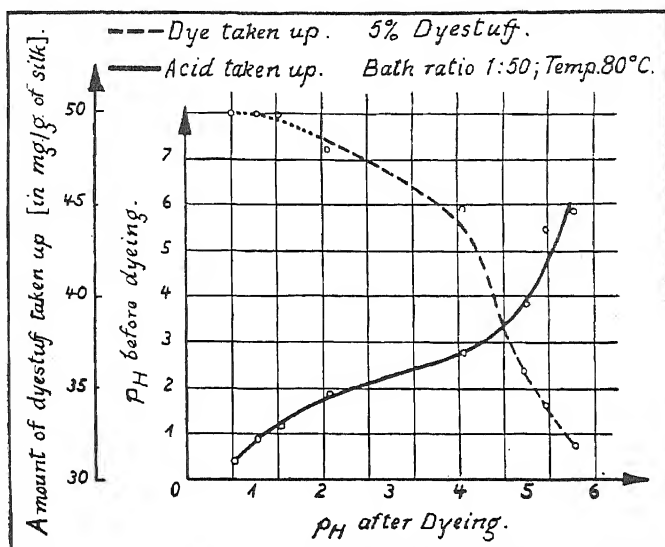


Fig. 2.—Amount of acid and dyestuff taken up by unloaded silk.
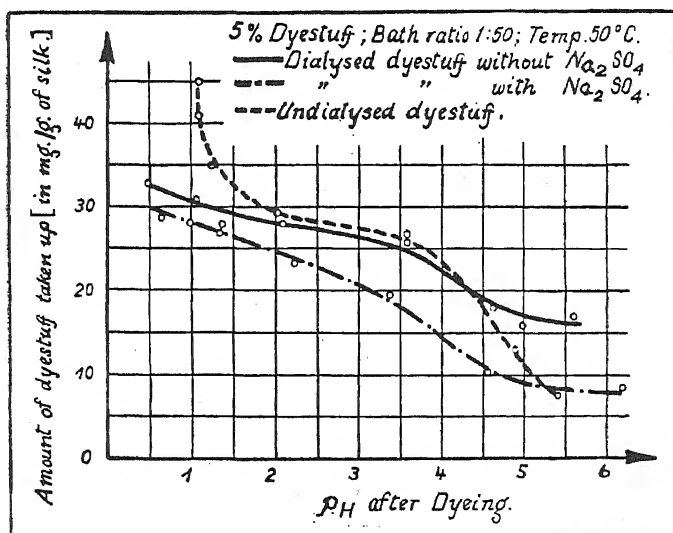


Fig. 3.—Amount of dyestuff taken up by unloaded silk.

theory of membrane equilibrium. One can trace the absence of a maximum to this masking.

It is interesting to note the influence of additions of salt upon the taking up of dyestuff. If sodium sulphate is added to a bath prepared with salt-free dyestuff, the taking up of dyestuff falls off ; this is especially noticeable in feebly acid conditions (Fig. 3). If one uses dye-baths with

unpurified (commercial) dyestuff (about 67 per cent. salt calculated on the weight of dyestuff) one finds a remarkable result.

In weak acid conditions (above $p_H = 3·5$) less dyestuff is taken up ; in strong acid conditions on the contrary it is increased. This effect can be explained as follows. In strongly acid conditions there occurs a flocculation of the dyestuff, which is still increased by the addition of salts. The amount of dyestuff taken up is thereby increased (in part adsorbed on the surface of the fibres). In feebly acid conditions the flocculation, provoked by the acid, is very slight, so that in this case the salts act differently and the amount of dyestuff taken up in the sense of the Donnan theory of membrane equilibrium, is restrained.

Whether an addition of salts lowers or raises the dyestuff affinity, appears to depend on several factors. One of these is the $p_H$ value of the dyebath. As suggested above the dyestuff affinity is decreased or increased by additions of salts according to the $p_H$ value of the bath. It is even probable that individual salts produce specific results. Sodium sulphate lowers the dyestuff affinity in feebly acid conditions, but in strong acid it is practically without any action, or lowers the affinity only slightly. The sodium chloride and sodium carbonate contained in undialysed dyestuff, on the other hand, raises the dyestuff affinity at a $p_H$ value which, with sodium sulphate alone, has practically no effect or which brings about only a very slight lowering of the dyestuff affinity. This result is much more surprising in view of the fact that a litre of dye-bath contains more salt by weight (3 grs. $Na_2SO_4$) than the undialysed dyestuff employed (2 grs. $NaCl + Na_2CO_3$ per litre of bath). The other factor, which influences the action of the salts, is the type of fibre.

## Experiments with Loaded Silk.

Technically loaded silks were then dyed with substantive dyestuffs. It was found that the loaded silk retains substantive dyestuff in a quite characteristic fashion. However much the loaded silk was dyed with the substantive dyestuff, it was impossible to follow the dyestuff absorption quantitatively in strongly acid concentrations (somewhat under $p_H = 3$) on account of the strong flocculation. The cause of the flocculation has

TABLE III.

| Experiment No. | $p_H$ Before Dyeing. | After | Amount of Dyestuff taken up in mg. per 1 grm. of Weighed Silk. | Taking up of Dyestuff in mg. per 1 grm. of Silk Substance. |
|---|---|---|---|---|
| 5 per cent. diamine-sky-blue FF calculated on the weight of pure silk. Bath ratio, 1 : 50. Temperature, 50° C. Ash content of the weighed silk, 46·86 per cent. | | | | |
| 1 | 3·70 | 3·70 | 7·60 | 15·00 |
| 2 | 5·52 | 4·05 | 6·60 | 12·40 |
| 3 | 6·45 | 4·37 | 1·55 | 2·90 |
| 4 | 7·42 | 4·65 | 1·30 | 2·45 |

already been pointed out above. In weaker acid or neutral conditions (over about $p_H$ 3·5) one can follow the taking up of dyestuff quantitatively, but in these conditions the loaded silk absorbs less dyestuff (calculated on the pure silk substance) than the unloaded. Loaded silk acts quite differently when dyed with *acid* dyestuffs. The taking up of acid dyestuffs (calculated on the pure silk substance) is much greater for loaded silk than for unloaded. As an explanation for this, it can be assumed that

the loading acts on the secondary valencies of the silk, or that the space
between the particles of the silk is filled in by the weighting substance,
so that the diffusion into the silk fibre of the colloidally dispersed
substantive dyestuff is hindered.   On the other hand the secondary valen-
cies as well as the space between the particles of the silk due to the diffusion
of the highly dispersed acid dyestuff should at the most play a subordinate
rôle.   In any case the dyestuff affinity is very slight, as Table III. shows.

In order to find out how the loading material reacts towards sub-
stantive dyestuffs, it was introduced in the substance itself.   A 25 per cent.
tin tetrachloride was for this purpose hydrolysed with a large quantity
of tap water and the precipitated stannic hydroxide rewashed.   The sus-
pension was then treated with a sufficient quantity of an 18 per cent.
sodium phosphate solution for half an hour at 60° C. and after several
washings introduced into a waterglass solution of 3° Bé. at 60° C.   After
half an hour the resulting precipitate was washed, and finally electrodialy-
tically purified and then used for the dyeing experiments.

The experiments were carried out as follows.   The dyestuff solutions
were divided into two parts, one of which was treated with the aqueous
suspension of the tin phosphate silicate, and the other with the same quan-
tity of conductivity water as was contained in the suspension liquid.   The
second solution served for determining the end $p_H$ value and the dyestuff
concentration.   The results of the experiment are given in Table IV.

TABLE IV.

| Experiment No. | $p_H$ | | | Amount of Dyestuff taken up in mg. per grm. of Preparation. |
| | Before Dyeing. | | After | |
| --- | --- | --- | --- | --- |
| 5 per cent. diamine-sky-blue FF calculated on the weight of the preparation. Bath ratio, 1 : 50.   Temperature, 50° C.   Reaction time, 1 hour. | | | | |
| 1 | 0·70 | | 1·00 | Total absorption |
| 2 | 1·05 | | 1·00 | ,, |
| 3 | 1·35 | | 1·32 | 49·50 |
| 4 | 2·15 | | 2·40 | 39·50 |
| 5 | 2·90 | | 2·80 | 11·30 |
| 6 | 3·90 | | 2·90 | 9·80 |
| 7 | 4·65 | | 2·92 | 8·50 |
| 8 | 6·40 | | 3·10 | 6·00 |

It is striking that the end $p_H$ values of the dye-bath remain of the order
of $p_H = 2\cdot80$ to $3\cdot10$ when the initial values lie above about $p_H = 2\cdot5$.
The above $p_H$ interval corresponds roughly to the isoelectric point of the
preparation.   The reaction of the preparation towards colourless solutions
having the end $p_H$ values of the dye-bath is peculiar.   The first three rows
of the experimental results give up absolutely no dyestuff ; the fourth row
a great deal, but slowly, and the fifth to eighth rows give up the greatest
part of the dyestuff.   As the isoelectric point shows, the preparation has
an acid character.   The acid nature of the preparation is also proved by
the fact that it takes up no acid dye from acid solution, in contradistinction
to basic from alkaline solution.   It was to be expected that the loading
material would also take up no substantive dyestuff in an acid bath, for
the substantive dyestuffs are themselves sulpho-acids.   The fact that,
nevertheless, the substantive dyestuffs are taken up in reasonable quantity,
in contradistinction to the acid dyestuffs, especially in strong acid conditions,
can be explained by the fact that the stannic hydroxide of the loading
material is colloidally soluble in the strongly acid solutions and that

the colloidal stannic hydroxide forms a difficultly soluble lake with the substantive dyestuff. The formation of this difficultly soluble lake prevents a quantitative estimation of the amount of dyestuff taken up by loaded silk in strongly acid solution. Since not all dyestuffs form difficultly soluble lakes with metals, it is understandable that the dyeing of loaded silk with acid dyes is quantitatively estimable and, further, that the loading material, as is to be expected, does not combine with the acid dyestuff.

### Experiments With Wool.

A further problem in this work was to find out whether substantive dyestuffs react towards wool in the same way as the acid dyestuffs. K. H. Meyer and H. Fickentscher [4] have found that wool has a lower equivalent weight than silk. It therefore follows from this that the wool should take up not only greater quantities of acid dyestuff but also greater quantities of substantive dyes, than the silk. Our researches have shown that wool does indeed take up more *acid* dyestuff, corresponding to its lower equivalent weight. Since the substantive dyes are sulpho acids, the ability to take up more dyestuff, as explained above, may be expected. On the other hand wool shows no fibre structure, in contradistinction to silk. It is therefore not to be expected that there should be such a strong secondary valency type of absorption of the substantive dyestuff as is the case with silk or, still more so, with cotton.

The assumption that the action of the secondary valencies of wool is not so marked as in the case of silk or cotton, has been plausibly substantiated by the important researches of Astbury [5] on the structure of wool. Wool possesses main chain valencies, which are joined together by the valencies of the side chains. The main chain valencies lie somewhat zig-zag and form a network with more or less secondary valencies jutting out at the sides. If the wool is stretched, the secondary valencies may be broken and for the most part temporarily freed and orientated alongside the main chain. If the wool fibres can fix substantive dyestuffs by means of their secondary valencies, then stretched wool ought in this transition stage to take up more dyestuff than unstretched. Since the substantive dyes, due to their secondary valencies, have a greater tendency to unite than the acid dyes, it was to be expected that the difference between stretched and unstretched wool would be better shown up when dyed with substantive dyes than with acid dyes. Experiments have proved this to be correct.

In addition to this explanation, another might also be justifiable. In consequence of the stretching, the scales of the wool fibre might become more detached and thus the pores of the wool are more accessible to the diffusion of the dyestuffs. By this process the velocity of the taking-up of dyestuffs might be increased. This, however, only partly agrees with the fact that by the stretching and the elongation of the fibre, the structure itself of the wool becomes closer. Our future experiments will decide this question.

### Experiments with Stretched Wool and Silk.

In order to discover whether there was any difference in dyeing affinity between stretched and unstretched fibres, the following experiments were carried out with stretched and unstretched wool and silk. For this, single fibres of wool or silk were stretched in a 5 per cent. solution of Marseilles soap at 50° C. to 55° C. In the case of wool the stretching was about 65 to 70 per cent. with the silk about 30 to 32 per cent. The silk cannot be stretched more as there is an elastic limit at about 35 per cent. At the same time loose wool and silk fibres were treated with the soap solution in order to prevent possible chemical reactions of the soap solution on the

[4] *Mell. Textilber*, 600, 1926; 781, 1927.
[5] W. J. Astbury, *Fundamentals of Fibre Structure*, London, 1933.

fibres in the comparative experiments.   The fibres, treated in this manner,
were thoroughly washed with distilled water and dyed with a o·1 per cent.
solution of the following dyestuffs.   Diamine-sky-blue FF, Brilliant
Geranine B., Brilliant wool blue 2 FR extra and Sulpho Rhodamine B.
Microscopical examination showed that the stretched wool takes up at
the same time considerably more dyestuff than the unstretched : between
stretched and unstretched silk, on the other hand, there was no difference.

An attempt was further made to measure the above results quanti-
tatively.   Large quantities of wool were stretched, as described above,
and compared in their properties with unstretched, but soap-treated,
fibres.   Part of the wool was steamed.   According to Astbury the stretch-
ing of wool is reversible, if the stretching does not exceed 70 per cent. and
one does not steam it, or only for a short time.   If the wool is stretched

TABLE V.

| Experiment No. | $p_H.$ Before Dyeing. | After | Amount of Dyestuff taken up in mg. per 1 grm. of Wool. |
|---|---|---|---|
| 5 per cent. dianil-true-scarlet GSN calculated on the weight of wool.   Bath ratio, 1 : 50.   Temperature, 80° C.   One hour. | | | |
| 1 | 2·12 | 3·15 | 15·60   stretched      } steamed |
| 2 | 2·12 | 3·15 | 9·70   unstretched |
| 3 | 2·12 | 3·20 | 15·50   stretched      } non-steamed |
| 4 | 2·12 | 3·20 | 8·00   unstretched |
| 10 per cent. crystal ponceau calculated on the weight of wool.   Bath ratio, 1 : 50.   Temperature, 50° C.   One hour. | | | |
| 1 | 2·00 | 2·47 | 69·30   stretched      } steamed |
| 2 | 2·00 | 2·47 | 64·00   unstretched |
| 3 | 2·00 | 2·47 | 59·00   stretched      } non-steamed |
| 4 | 2·00 | 2·47 | 60·50   unstretched |

over 70 per cent. and then is steamed in the stretched condition for two
hours, then the stretch is irreversible.   In order to check Astbury's dis-
covery, steamed and unsteamed stretched wool samples were dyed and the
length of the stretched wool was measured before and after dyeing.   For
the dyeing of the wool samples, in one case a o·1 per cent. solution of
Dianil-true-scarlet D.S.N. was used and in the other case a o·2 per cent.
crystal ponceau solution (Table V.).   The samples dyed with Dianil-true-
scarlet show that the stretched wool takes up substantially more dyestuff
as well in steamed as in unsteamed condition than the unstretched.   The
samples dyed with the acid dyestuff crystal ponceau show, on the contrary,
no such influence or in any case only a slight influence.   It is to be noticed
as well that the fibre length of the stretched wool sample remained un-
changed during the dyeing, i.e., that the stretch was irreversible not only
in the case of the steamed wool but also in that of the unsteamed.

## Influence of Swelling.

A further factor which can influence the dyeing affinities of wool and
silk is the swelling property of the fibres.   Swelling is caused by the fibre
micelles being forced apart.   Spaces are thus formed between the micelles,
which are small or large according to the degree of swelling.   It is quite
possible that the diffusion of the large molecular aggregates of the sub-
stantive dyestuffs is influenced by the inter-micellar space.   In other
words, the particles of the substantive dyestuffs can penetrate more easily
into the larger intermicellar spaces than into the smaller ones.

In order to clear up this question the amount of swelling and the amount of substantive dyestuffs taken up by wool, silk and hides are set out in Tables VI. and VII. in comparison. From these tables one sees that wool swells the least, silk more, but hides possess the highest capacity for swelling. The dyestuff affinity increases in the following order, wool, silk, hides, *i.e.*, wool which swells least shows the least affinity for dyestuff, the more readily swelling silk shows a substantially greater dyestuff affinity, and lastly the hides with the greatest degree of swelling show the greatest affinity for dyestuff.

We can base an explanation of the dyeing reactions upon this comparison as follows. When the fibres swell there are formed definite spaces between the particles into which the dyestuff enters, there to be combined with the fibre proteins. The greater the intermicellar spaces caused by fibre swelling, the more dyestuff can penetrate into the fibre. On the other hand, the absorption of dyestuff is also dependent on the size of the dyestuff particles.

TABLE VI.

| Experiment No. | $p_H$ Before Dyeing. | Degree of Swelling. | | |
|---|---|---|---|---|
| | | Wool. | Silk. | Hides. |
| 1 | 0·80 | | 1·511 | 7·80 |
| 2 | 1·00 | 1·468 | 1·512 | 5·55 |
| 3 | 1·36 | | 1·523 | 5·75 |
| 4 | 2·00 | 1·252 | 1·528 | 5·33 |
| 5 | 3·20 | 1·226 | 1·498 | 5·22 |

TABLE VII.

| Experiment No. | $p_H$ Before Dyeing. | Taking up of Dyestuff. | | |
|---|---|---|---|---|
| | | mg. per grm. Wool. | mg. per grm. Silk. | mg. per grm. Hide. |
| 1 | 1·19 | 35·80 | 50·00 | 208·0 |
| 2 | 2·13 | 22·00 | 48·00 | 150·0 |
| 3 | 2·85 | 12·00 | 44·80 | 79·0 |
| 4 | 4·00 | 4·00 | 36·00 | 53·0 |
| 5 | 6·62 | 3·00 | 31·80 | 40·0 |

A compact molecular dispersion of dissolved dyestuff (independent of the degree of swelling of the fibres) is absorbed by the reaction capacity of the fibre proteins, because such dyestuff, independently of the degree of swelling, can penetrate easily into the fibre. The colloidal substantive dyestuffs cannot penetrate into the fibres so readily on account of the greater size of their particles.

It is thus understandable that the more reactive wool takes up less substantive dyestuff than the less reactive silk. The diffusibility of the dyestuff being decisively influenced by the swelling, predominates over the reactivity of the individual fibres, so that they cannot take up the amount of substantive dyestuff corresponding to their reactivity.

(It is to be remarked that the hides were dyed for 16 hours at a temperature of 35° C. with dianil true scarlet GSN, the wool and silk, however, being dyed with diamine-sky-blue FF at 80° C. for one hour. The swelling of the wool and silk was measured at 50° C., that of the hide at 35° C.)

## Influence of the Addition of Neutral Salts on the Taking up up of Dyestuffs.

According to discoveries by E. Elöd and F. Böhme the absorption of acid dyestuffs by wool is gradually diminished by increasing additions of neutral salts to the dye-bath.    These facts can be explained with the help of the deductions drawn from the membrane equilibrium.    According to Donnan the distribution of a salt AB between fibre protein and solution follows the equation.*

$$\frac{(AB)a}{(AB)i} = 1 + \frac{c_1}{c_2} = \lambda$$

If the solution of a second salt is added then the relation $\frac{(AB)a}{(AB)i} = \lambda$ is

diminished.    If $c_1$ and $c_2$ stand for dyestuff concentrations and $c_3$ the concentration of a second salt solution, then one arrives at the relation

TABLE VIII.

| Experiment No. | $p_H$ Before Dyeing. | After | Amount of Dyestuff taken up in mg. per 1 grm. Wool. |
|---|---|---|---|
| | Without sodium sulphate. | | |
| 1 | 0·50 | 0·62 | 1·80 |
| 2 | 1·10 | 1·05 | 1·60 |
| 3 | 1·48 | 1·55 | slight  dyestuff  absorption not   measurable   colorimetrically. |
| 4 | 1·95 | 2·57 | |
| 5 | 3·00 | 4·00 | |
| 6 | 3·80 | 5·00 | |
| | With 15 per cent. sodium sulphate calculated on the weight of wool. | | |
| 1 | 0·70 | 0·87 | 1·50 |
| 2 | 1·00 | 1·05 | 1·00 |
| 3 | 1·40 | 1·70 | slight  dyestuff  absorption not   measurable   colorimetrically. |
| 4 | 2·15 | 3·10 | |
| 5 | 2·90 | 4·70 | |
| 6 | 4·05 | 5·35 | |

$\lambda = 1 + \dfrac{c_1}{c_2 + c_3}$.    With  increasing  additions  of  salts, however, the dye-stuffs are more and more flocculated.    There is then the possibility that by a sufficiently long action of the dye-baths the dyestuff affinity will be compensated, *i.e.*, that after a long time there will be as much dyestuff taken up from the salt-containing bath as from a salt-free bath.    In the present work it is also sought to clear up this question.    It was to be expected that the relations when dyeing wool with substantive dyestuffs would be the same as when using acid dyestuffs.    To our great astonishment however it turned out that this was not so.    Wool was dyed with 5 per cent. diamine-sky-blue FF at 50° C. for one hour in a bath with proportions of 1 to 50. The experiments were carried out with and without additions of sodium sulphate.

If one compares Table VIII. with Table I. it is seen that whereas the silk takes up a large quantity of substantive dye, wool, under the same conditions, is scarcely dyed.

* $c_1$ = AB concentration in the fibre.
  $c_2$ = AB concentration in the solution.
  $\lambda$ = relation figure.

In further experiments the temperature was raised from 50° to 80° C.,, other conditions remaining the same.   Table IX. shows that wool has now taken up quite appreciable quantities of dyestuff.   If, however, Table IX. is compared with the third and fourth parts of Table I., it is seen that wool still takes up less dyestuff than silk, under the same conditions. It is interesting to note that the quality of the wool dyeing is better than that of the silk.   As is to be seen, furthermore, wool liberates only an unmeasurable quantity of dyestuff, while silk, especially in feebly acid conditions, liberates measurable quantities.   Probably the combination between wool and dyestuff is less easily dissociated than that between silk and dyestuff.   On the other hand it is also possible that the adsorptive combination in the case of the more strongly reacting wool, with its surface particle structure different from that of silk, is stronger than in the case of the less reacting silk.   Thus the adsorbed dyestuff in the case of wool is discharged less than in the case of silk.

TABLE IX.

| Experiment No. | Before Dyeing. | $p_H$ After | Amount of Dyestuff Taken up in mg. per 1 grm. Wool. | Dyestuff Liberated in mg. per 1 grm. Wool. |
|---|---|---|---|---|
| 5 per cent. diamine-sky-blue FF calculated on the weight of wool.   Bath ratio, 1 : 50.   Temperature, 80° C. ||||
| 1 | 0·47 | 0·55 | 38·20 | traces |
| 2 | 0·90 | 1·00 | 40·00 | ,, |
| 3 | 1·20 | 1·33 | 35·80 | ,, |
| 4 | 1·90 | 2·50 | 22·00 | ,, |
| 5 | 2·82 | 4·40 | 12·00 | ,, |
| 6 | 3·85 | 5·33 | 4·0C | ,, |
| 7 | 5·45 | 5·40 | 4·00 | ,, |
| 8 | 5·80 | 5·95 | 3·00 | ,, |
| 5 per cent. diamine-sky-blue FF + 15 per cent. $Na_2SO_4$ calculated on the weight of wool.   Bath ratio, 1 : 50.   Temperature, 80° C. ||||
| 1 | 0·47 | 0·65 | 33·00 | traces |
| 2 | 0·90 | 1·03 | 31·00 | ,, |
| 3 | 1·20 | 1·45 | 25·20 | ,, |
| 4 | 1·90 | 3·02 | 15·20 | ,, |
| 5 | 2·82 | 4·90 | 2·80 | ,, |
| 6 | 3·85 | 5·60 | slight | ,, |
| 7 | 5·45 | 6·00 | ,, | ,, |
| 8 | 5·85 | 6·25 | ,, | ,, |

In the case of wool also dyeing was carried out with dialysed and un-dialysed dyestuffs.   The researches showed a similarity with those corresponding with silk.   Large quantities were absorbed by the undialysed dyestuff.   The difference in dyeing affinity between wool and silk is also shown up here.   Wool takes up less dyestuff than silk.

A comparison of the dyeing affinity of silk and wool affords an interesting study.   The dyeing affinity of wool is, like silk, dependent on the hydrogen ion concentration.   On the same grounds as in the case of silk, one cannot obtain a maximum for the amount of dyestuff taken up.   As in the case of silk, the reactions of salt containing baths on the dyeing affinity are the same.   On the other hand, both sorts of fibre show great differences in the absolute quantity of dyestuff taken up.   Wool is scarcely dyed at low temperatures (50° C.) and even at higher temperature does not attain the dyeing affinity of silk.   Actually the reverse was to be expected.

In the experiments on silk, on the other hand, no influence could be observed by the salt solution.   One can suppose that the addition of salts

brings about a slight increase in the particle size of the dyestuff. It is further possible that highly orientated silk fibres retain the dyestuff firmly at this $p_H$ value (2·00) not only chemically by their amino groups, but also by means of the secondary valencies, unless the particles of the acid dye-stuff are too large. Thus a greater absorption of dyestuff takes place, which counteracts the expected lowering of the dyestuff affinity. The action of the secondary valencies is slight in the case of wool and hides, and, in consequence, the lowering of the dyestuff affinity is clear. As is to be seen from the dyeing experiments on silk with substantive dyes, it is possible that with high $p_H$ values (approx. 3-4) the lowering of the dyestuff affinity is caused by the addition of neutral salts.

The values for $\lambda$ calculated on the experimental data show that only in the case of wool and hides is there a complete agreement between calculation and actual dyestuff absorption, i.e., $\lambda$ is smaller as the corresponding dyestuff absorption is less. On the other hand, the values for $\lambda$ calculated for silk on the experimental data are lower, while the dyestuff absorption results arrived at experimentally are practically unaltered.

A further difference between the relations of wool, silk and hides lies in the speed with which dyestuff is taken up. Experiments at 20° C. show that the taking up of the dyestuff by wool is only complete after 96 hours, while the end point for silk is reached after 8 hours and for hides after 12 hours. At 50° C. also these differences between wool and silk are clear and distinct. Likewise they can be seen when sodium sulphate is present in the dye-bath.

# THE PROTEINS AS COLLOIDAL ELECTROLYTES.

By Dorothy Jordan-Lloyd.

Considered as types of colloidal electrolytes, the proteins have a number of very definite and outstanding characteristics. In the first place they are amphoteric and can therefore act as kations or anions according to circumstances. Not only that but when ionised they form zwitterions, thus carrying at the same time both positively and negatively charged centres. The groups which are capable of acting as positively charged centres, that is the basic groups, all contain nitrogen atoms. They are *amino groups* arising from the lysine or hydroxylysine residues in the main polypeptide chain, *guanidine groups* from the arginine residues and *imino groups* from the histidine residues. Moreover since it has been shown on various occasions that these groups are insufficient to account for all the acid that can combine with proteins, it seems possible that in high concentrations of strong acids the imino groups of the polypeptide links may also function as charged centres (Jordan Lloyd and Mayes, Prideaux and Woods, Czarnetsky and Schmidt, etc.).

The groups which are capable of acting as negatively charged centres, that is the acidic groups, are the carboxyl groups arising from the glutamic and aspartic acid residues of the polypeptide chain and the hydroxyl groups of the tyrosine and other hydroxy acids.

Figure I (from Jordan Lloyd) shows the $p_H$ ranges over which these various groups of these basic or acidic amino acids are in the charged or neutral condition respectively. It should be noted that the figures

FIG. I.
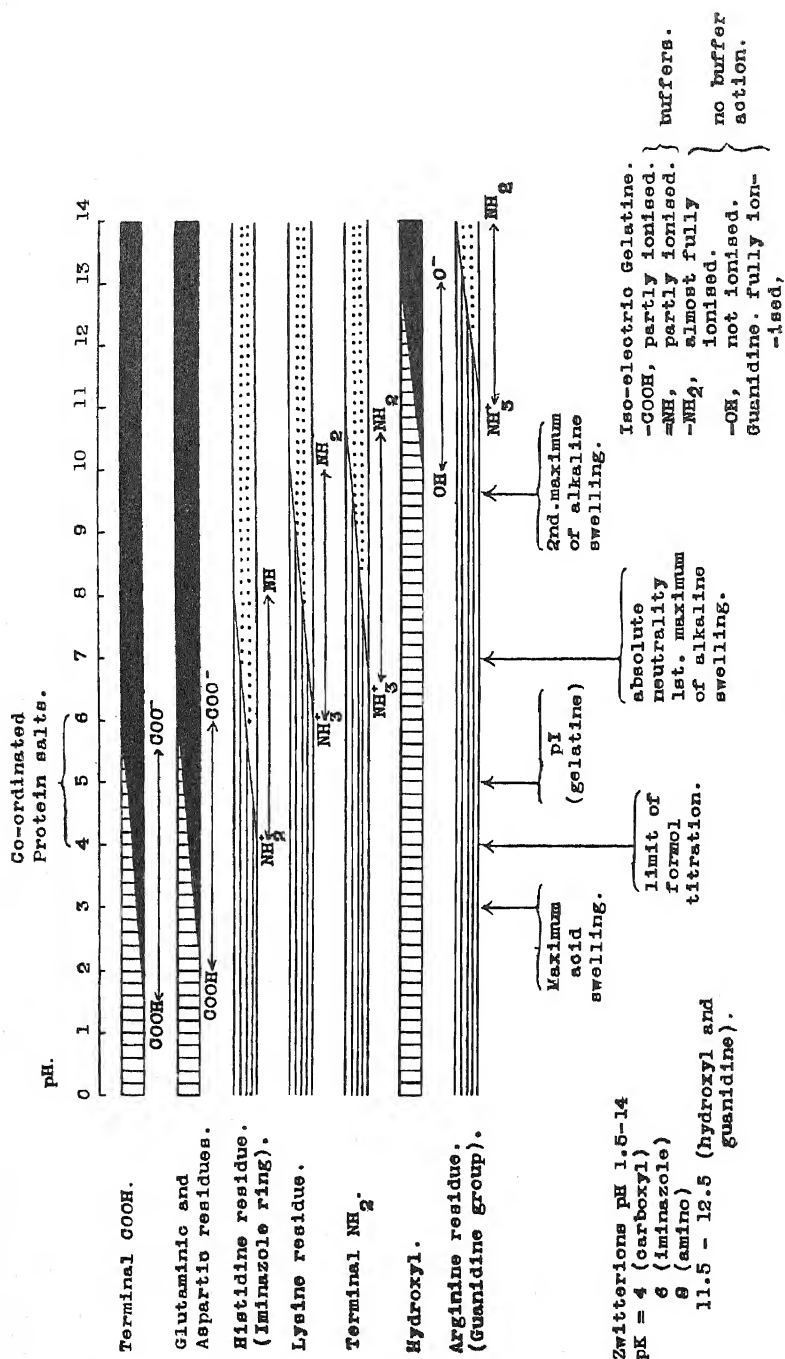
given refer to values found for these groups in the free amino acids, but that the values for the amino and carboxyl groups of the $\alpha$-carbon atom have been excluded since these two latter are not present as free groups in the protein molecule. The values given for the groups in the free amino acids are doubtless shifted to some extent to the right or left when the groups are in position as side chains of the protein molecule. However, judging by the few titrations of proteins which are available, this shift is only slight for most of the groups.

The electrolytic character of the proteins therefore can be explained by their constitution. Since the protein molecule contains upwards of 200 amino acid residues condensed into a long polypeptide chain, the number of positively and negatively charged centres which any one molecule may contain may be very large. It is rather a moot point whether it is more profitable to regard the protein molecule as a single multi-valent ion or whether to regard each charged centre as a single mono-valent ionised centre. Probably a rigid point of view on this matter is best avoided. In the molecule of silk fibroin, where the fully extended zig-zag pattern of the backbone has been demonstrated by X-ray analysis, and where the charged centres are notably few, it seems highly probable that each one of these acts as an independent unit. In other proteins, however, the charged centres are more numerous and the backbone of the molecule is apparently thrown into loops on coils. In these cases a number of charged centres of the same sign may be brought into close approximation forming a sort of multi-valent centre. Or if several side chains of R groups giving rise to charged centres are placed close together in the polypeptide chain, one may again get something which can be regarded as a multi-valent centre.

Before leaving the subject of the charged centres or, if it is preferred, the ionised centres, in protein molecules, it is important to realise that though the existence of the zwitterion has been proved beyond reasonable doubt, it must not therefore immediately be taken for granted that the positively and negatively charged centres will behave on exactly similar lines to the cations and anions of a simple electrolyte, say sodium chloride. For one thing the ionised centres of the zwitterion are not free to move as individuals. The positive ion of sodium apparently exists in the crystalline salt surrounded at equal distances by six negative chlorine ions, each of which can equally be regarded as surrounded by six sodium ions. In solution, though the ions are moving freely, this spatial pattern, by which electric neutrality is maintained throughout the system, still exists. The positive centres of a protein molecule obviously cannot, for spatial reasons, take up an equally symmetrical position with regard to any anions. It is possible that this simple fact explains a great deal. For instance it is well known that if two salts which ionise to form pairs of independently moving ions, say NaCl and KBr, be dissolved together and then crystallised out, the solution will give a mixed crop of crystals containing not only sodium chloride and potassium bromide, but also sodium bromide and potassium chloride. It is also known that amino acids dissolved in water containing in solution salts of the alkali or alkaline earth metals will form crystalline compounds with these salts, in other words a redistribution of the cations and anions takes place in the system (Boussingault, Horsford, Pfeiffer and Modelski) This redistribution, however, is not a simple crossing over of positive and negative ions from the two constituents as in the case of the simple crystalloids, since there is an alteration in the strength of both acidic and

basic groups (Leuthardt) and the formation of co-ordination complexes at the amino groups has been suggested as follows :—

$$COO^- . P . NH_3^+ + Me^+ + X^- \rightarrow COO^- . P . NH_2 . MeX + H^+$$
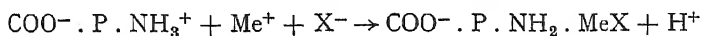
Evidence that the change is of this type comes from titration curves of amino acids in the presence of salts such as $MgCl_2$. Apparently amino acids, simple peptides and proteins (Leuthardt, Pauli) all show this same effect.

Double salts of amino acids and ordinary salts of the type $Me^+ COO^- . P . NH_3^+ X^-$ have indeed been postulated but have never been shown to exist though amino acid derivatives of the types $Me^+ COO^- . P . NH_2$ and $COOH . P . NH_3^+ X^-$ are known to occur, for example copper salts and picrates, both of which are used for separating the amino acids in a pure state.

The combination of the ions of an electrolyte with a zwitterion seems to rest on the suppression of one of the charged centres of the zwitterion. Proteins in the iso-electric condition have never been proved to combine by means of electro-valent links simultaneously with both ions of salts. Loeb's original experiment showing that cations only combine with proteins when the latter have a predominating anionic charge (*i.e.*, in alkaline solution) and that anions only combine with proteins when the latter have a predominating cationic charge (*i.e.*, in acid solution) has been many times confirmed. Indeed the method of determining the iso-electric point of a protein by means of positively and negatively charged dyes is based on this assumption. We are forced, therefore, to the conclusion that though proteins form zwitterions in solution, the charged centres have not that freedom of action found with the ions of crystalloids of the more familiar type.

The charged centres of the protein zwitterion exist in electrostatic balance with each other and apparently this balance can only be disturbed by some mechanism which can suppress either the positive or the negative charge. Outstanding in its effect is the hydrogen ion. This can co-ordinate either with $-COO^-$ making $-COOH$ and leaving $-NH_3^+$ free to react or it can be removed from co-ordination with $-NH_3^+$ leaving $-NH_2$ and $-COO^-$ free to react. The transference of the hydrogen ion from one position of co-ordination to another depends on the $p_H$ value of the solution :—

$$COO^- . P . NH_3^+ + H^+ \rightarrow COOH . P . NH_3^+ \text{ (in acid solution).}$$
$$COO^- . P . NH_3^+ - H^+ \rightarrow COO^- . P . NH_2 \text{ (in alkaline solution).}$$
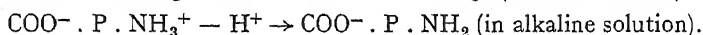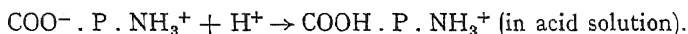
Once the *zwitterion* partnership has been broken numerous other ionic reactions can occur. All the electro-valent reactions of proteins take place either in acid or alkaline solutions. The fact that the ionic centres shown to exist in the protein are, as it were, anchored at definite positions in a long stable molecule surely plays a leading part in enforcing the apparent electrolytic inertness of proteins at the iso-electric point.

The influence of the size and structure of the molecule on its properties brings us to the consideration of the proteins as colloids. It is well known that proteins have enormous molecules. The molecular weights appear to start at values of about 34,000 and to rise as multiples of this, the respiratory proteins having molecular weights running into millions. The colloidal nature of the proteins therefore needs no other explanation. The relations of such large molecules to the molecules of

solvents is of great importance—unless the protein molecules are held apart by electric charges or by association with solvent molecules, they will tend to run together and hold with Van der Waals or other forces. Protein molecules in contact with water, have, as we have seen, charged centres and it is well known that they are most easily precipitated from solution at their iso-electric points.   Many proteins, however, are freely soluble in water at their iso-electric points.   Apparently such proteins have definite hydration centres localised in the side chains or R groups which are due to the presence of groups containing oxygen or nitrogen atoms (Jordan Lloyd and Phillips).   It appears likely that the molecules co-ordinate with water at hydroxyl, amino, imino and carboxyl groups. The proteins are hydrated colloids in aqueous solution.   The hydration may be partly due to water held by definite co-ordinate bonds to certain definite positions in the molecule and partly to the orientation of water molecules round charged centres.

There is no doubt that the hydration centres in colloids and the charged centres are closely related and that any electrolytic action in which a protein takes part influences its hydration.

A good illustration of this is found in the interaction of a charged protein and a colloidal ion of opposite sign such as occurs in tanning.

Reduced to its simplest form and ignoring the influence of biological structure, tanning may be imagined as occurring in the following stages :—

$$COO^- \, . \, P \, . \, NH_3^+ \, + \, [\text{tannin}]O^- \, + \, H^+$$
$$\downarrow$$
$$COOH \, . \, P \, . \, NH_3^+ \, + \, [\text{tannin}] \, O^-$$
$$\downarrow$$
$$COOH \, . \, P \, . \, NH_3 \, . \, [\text{tannin}] \, O$$
$$\vdots$$
$$\downarrow$$
$$COOH \, . \, P \, . \, NH \, [\text{tannin}] \, + \, H_2O.$$
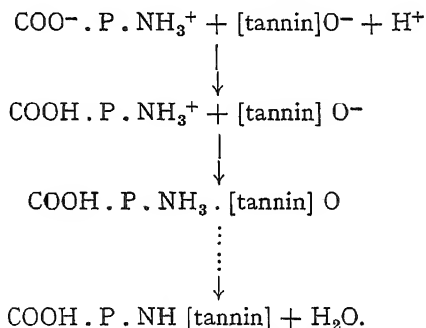
The chemistry of the tanning process illustrates two very important points when viewed from the standpoint of colloidal electrolytes.

The first point is that before any action can occur between the positively charged centres of the protein zwitterion and the negatively charged colloidal tannin, the partnership between the positive and nega-tive centres of the protein zwitterion must be broken by the action of hydrogen ions.   Few of the tannins are sufficiently acidic to bring this about and therefore some other acid has to be present in the system.   Any fairly strong acid is satisfactory.   In commercial tanning practice, sul-phuric acid or lactic acid, or a mixture of both, are used.   The interaction between collagen and tannins is in the first place undoubtedly electrolytic. Afterwards covalent bonds are formed with elimination of water co-ordinated at both interacting centres.   That part of the story is, how-ever, beyond the scope of this paper.

The second point, and this is very important for the present discus-sion, is the fact that tannins can instantaneously displace even such a strong acid as hydrochloric acid from gelatin chloride (Thompson).   The evidence for this is derived from the experimental observation that gelatin

chloride at $p_H$ 4·17 mixed with a solution of a tanning agent at $p_H$ 4·17 will give a precipitate of gelatin tannate with a fall in the $p_H$ of the solution to 4·02. The explanation of this appears again to lie in the structural properties of the large colloidal protein molecule. The matter can be approached in a hypothetical manner :—

If the molecules or ions of two interacting substances come together, the forces of the valency bonds (either co-valent or electro-valent) will tend to hold them together and the vibrational forces due to the kinetic energy of the individual molecules or ions will tend to shake them apart. But since all molecules (or ions) in equilibrium have the same kinetic energy, small molecules will be vibrating much more violently than large ones. Hence, if tannins, which have large molecules which give rise to large anions, find themselves in a system containing gelatin chloride or sulphate, which gives rise to large cations, there will be a definite re-arrangement of ions in the system such that the large negative ions of the tannins become associated with the large positive ions of the protein and free hydrochloric or sulphuric acid appears in the system leading to a definite fall in the $p_H$ value.

The influence of structure on stability does not end here for tannins differ in the strength of the forces with which they can hold a protein molecule, and strong tans can displace weak tans just in the same way that almost any tan can displace a non-colloidal acid. The strength of the bond between tannin and protein is described as the " astringency " of the tannin and my colleagues, Dr. Phillips and Dr. Humphreys, have brought forward evidence showing that astringency is directly related to molecular size. Now it must be borne in mind that proteins in acid solution have many positive centres and tannins, particularly those with large molecules, have many negative centres. If conditions are such that more than one pair of positive and negative centres come into electrostatic balance, the two ions will be held in position with forces which increase very rapidly with the increasing number of bonds. This principle, which has been made use of by Astbury in explaining the strong lateral cohesive forces which held the molecules in fibres, can be illustrated by a diagram :—

*Cohesion of Large and Small Ions.*
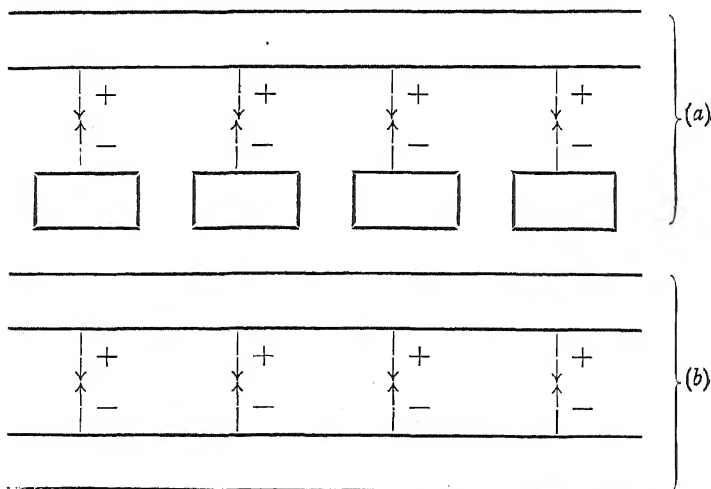


$(a)$ is less stable than $(b)$.

The consideration of proteins as colloidal electrolytes therefore brings out very forcibly the influence of molecular structure on chemical behaviour. In considering the chemistry of the crystalloids, the influence of the bulk of the molecule on the behaviour of particular active groups or centres is not always obvious, but as soon as the attention is turned to large colloidal molecules, containing a number of active centres held into fixed positions, then it becomes very clear that the size and structure of the molecule as a whole has a strong influence on the behaviour of every one of the active centres.

In conclusion we may illustrate this point by reference to the titration curves of gelatin and collagen which are shown in Fig. 2. These are taken from the paper of Atkin and Douglas and from some unpublished
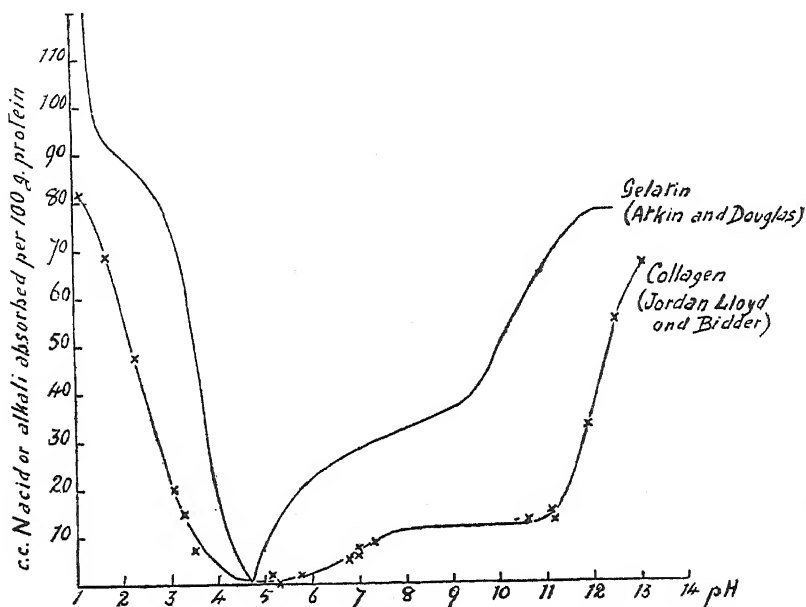


FIG. 2.

work of the author and Miss Bidder. The two proteins concerned are constitutionally the same, in fact gelatin is derived from collagen. Electrochemically their behaviour shows a strong contrast which can only be explained by the very different structural organisation of the two colloids.

REFERENCES.

Atkin and Douglas, *J. Inter. Soc. Leather Tr. Chem.*, 8, 359, 1924.
Astbury, *Fundamentals of Fibre Structure*, London, 1933.
Boussingault, *Ann. Chem.*, 39, 310, 1841.
Czarnetsky and Schmidt, *Ann. Rev. Bioch.*, 2, 1933.
Horsford, *Ann. Chem.*, 60, 1, 1846.
Jordan Lloyd, *J. Int. Soc. Leather Tr. Chem.*, 17, 245, 1933.
Jordan Lloyd and Mayes, *Proc. Roy. Soc. B.*, 93, 69, 1922.
Jordan Lloyd and Phillips, *Trans. Faraday Soc.*, 29, 132, 1933.
Leuthardt, *Helv. Chem. Acta.*, 15, 540, 1932.

Loeb, *Proteins and the Theory of Colloidal Behaviour*, New York, 1922.
Pauli, *Hofmeistr. Beita*, **5**, 41, 1904.
Pfeiffer and Modelski, *Z. Physioll Chem.*, **81**, 329, 1912.
Pfeiffer, Wittka and Wurgler, *Ber.*, **48**, 1938, 1915.
Phillips, *J. Int. Soc. Leather Tr. Chem.*, **18**, 165, 1934.
Phillips and Humphreys, *J. Int. Soc. Leather Tr. Chem.*, **18**, 178, 1934.
Prideaux, *Proc. Roy. Soc. B.*, **108**, 224, 1931.
Prideaux and Woods, *Proc. Roy. Soc. B.*, **110**, 353, 1932 ; **111**, 201.
Thomson, *J. Int. Soc. Leather Tr. Chem.*, **18**, 175, 1934.

# SOME ELECTROCHEMICAL PROPERTIES OF A SIMPLE PROTEIN.

By K. Linderstrøm-Lang.

During the last ten to fifteen years our knowledge of the constitution of the proteins has undergone considerable development. As a result of physical investigations and chemical analysis (including as an important part enzymatic analysis) of these substances of high molecular weight we can now, with a certain reservation, describe them in the following way.

The protein molecule consists mainly of amino-acids linked in an unbranched or, in some rare cases, a branched *chain*. The principal bond is the peptide link into which enter only the carboxyl groups and the α-amino groups—or eventually the α-imino groups from such amino-acids as proline and hydroxy-proline. Other nitrogen-containing groups are free, *e.g.* the guanido groups in arginine, the imidazol group in histidine, the ε-amino group in lysine. In monoamino-dicarboxylic acids the carboxyl group not entering into the peptide chain is free, or is bound to ammonia with formation of an acid amide.

Now, it is important in the first place for the present problem to specify the *acidobasic* groups in the protein molecule, *i.e.* the groups capable of taking up or giving off hydrogen ions. They may be grouped as follows :—

1. The free α-amino group (or α-imino group) and the free carboxyl group at the ends of the peptide chain.

2. The free nitrogen containing groups in the amino acids mentioned above and the free carboxyl groups of the monoamino-dicarboxylic acids.

3. The hydroxyl and the sulphhydryl groups in the hydroxy-amino-acids including tyrosine, and in cysteine.

4. The peptide bonds.

5. Inorganic constituents of the protein molecule not mentioned above and of little interest for the present paper, *e.g.* phosphoric acid.

The question then arises, how the hydrogen ionisation of a given protein may be computed from its content of the various amino acids, if we assume that the ionisation constants of each of their specific groups are known in their uncombined state.

The solution of this problem presents several difficulties, the most important of which are :

Lack of complete analysis of most proteins.

Insufficient knowledge of the arrangement of the different amino acids in the chain, and partly due to this, an insufficient knowledge of

the change in electrochemical properties of the free acidobasic group (or groups) in an amino acid, produced by its linkage in the protein chain.

Finally, difficulties arising both from the colloidal properties of the proteins, involving association of several peptide chains to larger aggregates, and from interionic forces.

Several interesting attempts have been made to carry through such calculations (see Cohn,[6] Simms [24] and others), but, for the reasons mentioned, the results have so far been more qualitative than quantitative, and have mainly served to support the general view that it is possible to account for most of the acidobasic properties of proteins on this basis, a result which naturally must not be undervalued (compare [15, 16]).

As may be seen from the nature of the above-mentioned difficulties an investigation of a simple protein chain, of comparatively well-known composition, and which cannot form association products, would be of considerable interest. Therefore, when the study of clupein, the basic protein of herring's sperm, was taken up in this laboratory by S. P. L. Sørensen and given into the hands of K. E. Rasmussen the author proposed that an investigation of its acidobasic properties be undertaken. The results of this investigation are given elsewhere.[23] The data given below are extracted from this paper, but detailed references to the literature may be found in the original paper. Although the investigation has so far contributed but little to the solution of the strictly quantitative side of the above-named problem, some of the results obtained throw light upon the structure and the acidobasic properties of the proteins.

## A. General.

Clupein when obtained as crude preparation from dried sperm (see [22]), is a mixture of several proteins of very nearly the same structure. A high arginine-content is characteristic of them all and to this they owe their strongly basic properties, and their lack of other amino-acids save monoamino-monocarboxylic acids (M) of which the following have been isolated :

| | |
|---|---|
| Alanine | Serine |
| Valine | (Hydroxyvaline) |

and monoimino acids (for the sake of simplicity, also denoted by M)

Proline and Hydroxyproline.

Owing to the inhomogeneity of the ordinary clupein preparations nothing definite can yet be said about the percentage of these amino acids in the single proteins, but, as an average, the following figures may hold good :

Arginine (A) 88-92 per cent. A-Nitrogen of Total-N

M 12-8 per cent. M-Nitrogen of Total-N.

This roughly corresponds to 2 to 2·5 molecules of arginine per molecule of monoamino-monocarboxylic acid.

The structure of the chains may be assumed to be of the type [20]

$$-MAA-MAA-MAA-,$$

or in some cases

$$-MAA-AAM-AAM-AAAA.$$

At the amino end of the chains there is probably situated a molecule of M ; at the carboxyl-end, almost certainly an arginine molecule.

As mentioned above, the guanido-groups of the arginine molecules are free, and it may be assumed that at hydrogen ion concentrations above $10^{-9}$ (see later) they are completely ionized in aqueous solution

The values for the molecular weight ascribed to this protein have varied from 1000 to 3000 and no definite proof has been given for any of these figures.[9, 14, 29]   The heavy charge of the molecule makes the physico-chemical estimations (osmotic pressure, centrifugation) somewhat difficult.[12, 17, 29]   On the other hand it must be expected that such measurements when duly corrected for interionic forces are likely to give the true average molecular weight of the single chains because the charge on the single chains will probably prevent any measurable formation of association products.

## B. Investigation of a Nearly Pure Clupein Component.

1. By fractionation in a suitable way[22] the crude clupein mixture may be separated into several fractions with slightly different chemical composition. Some of these fractions behave like pure, or nearly pure, substances. Therefore a description of one of these nearly pure fractions[22] will be given.

Fraction No. 6 was obtained as a sparingly soluble sulphate. Its analysis is given in Table I.

TABLE I.—ANALYSIS OF FRACTION 6.

| Water Content Per Cent. | Total N Per Cent. | Sulphuric Acid. Per Cent. | Per Cent. of Total N. | |
| --- | --- | --- | --- | --- |
| | | | Humin-N. | Arginine-N. |
| 0·99 | 23·56 | 20·05 | 0·1 | 91·7 |

(see [22] and the more detailed paper [28]).   The ash content was negligible. The sulphate was dissolved in water at 40° and transformed into the chloride with the calculated amount of $BaCl_2$ with addition of a little HCl.   To the solution thus obtained was further added KCl so that its final composition was :

Solution A
$\begin{cases} \text{grams of clupein per 5 c.c.} = 0\cdot1891 \\ \text{KCl} \qquad\qquad 0\cdot1 \; N \\ \text{HCl (free and combined with clupein) about } 0\cdot22 \; N \\ \qquad pa_H \text{ (see [4]) } 2\cdot07. \end{cases}$

To bring 5 c.c. of this solution to the neutral point approximately 92 cu. mm $N/1$ NaOH (added from a microbürette[19]) were required.   The neutralised solution was titrated, partly with base in alcohol (indicator thymophthalein [10, 13, 30] and partly with acid in acetone (indicator naphthyl red.[18])   The quantities of base and acid required for these titrations were, per 5 c.c. original solution,

base, 44 cu. mm. $N/1$ ;
acid, 47 cu. mm. $N/1$.

Therefore, if we assume that the titration methods used give correct results in the present case, the number of equivalents of free amino groups (imino groups) and carboxyl groups per gr. of clupein be

$\dfrac{44 \times 10^{-6}}{0\cdot1891} = 2\cdot4 \times 10^{-4}$ and $\dfrac{47 \times 10^{-6}}{0\cdot1891} = 2\cdot5 \times 10^{-4}$ respectively.

Now, as the arginine groups are completely ionised and remain so during the titrations [20] and, as the peptide bonds and the hydroxyl groups remain unionised, the only reasonable explanation of the observed correspondence between the two titration values is that it is the free acidobasic groups at the ends of the open protein chain which have been estimated. We may therefore deduce from this that the average molecular weight of this clupein fraction is very nearly 4000 ($1/(2\cdot5 \times 10^{-4})$), from which it

follows (compare Table I.) that it must contain as an average 20 molecules of arginine, and 8 molecules of monoamino-monocarboxylic acid per molecule. In aqueous solution the chains have twenty positive charges in their amphoionic state.



Fig. 1.

This brief and approximate calculation is given in order to facilitate the understanding of the following treatment. In order to obtain accurate figures we shall have to proceed in another way. Fig. 1 gives the most likely structure of the chain but the arrangement of the inner groups is uncertain.

## 2. Electrometric Titration.

5 c.c. of solution A were titrated electrometrically at 18° with $N/1$ NaOH added from a microburette, having the volume 100 cu. mm. and graduated in 0·2 cu. mm. The hydrogen electrode was used (760 mm. pressure). Since the total quantity of base required to bring the $pa_H$ of the solution from 2·07 to 9·39 (at which stage the titration was stopped),

TABLE II.—37·82 GRS. OF CLUPEIN PER LITRE. [$C_T = 0.916 . 10^{-2}$]

| Cu. mm. $N/1$ NaOH per 5 c.c. Sol. A. | $c_{HCl} \cdot 10^2$ | $c_{NaOH} \cdot 10^2$ | $pa_H$ | Correction for Liquid Junction Potential | Equivalents Bound per Mol. of Clupein. | | $p_B$ | $p_S$ |
|---|---|---|---|---|---|---|---|---|
| | | | | | HCl. X. | NaOH. Y. | | |
| 0 | 1·798 | | $2·07_1$ | $+0·03_1$ | 0·913 | | $[3·09_2]$ | |
| 5·60 | 1·686 | | $2·11_1$ | $0·03_2$ | 0·883 | | $[2·99_9]$ | |
| ×16·72 | 1·464 | | $2·22_9$ | $0·03_3$ | 0·867 | | $3·04_3$ | |
| 29·58 | 1·206 | | $2·39_5$ | $0·03_6$ | 0·819 | | $3·05_1$ | |
| 41·81 | 0·962 | | $2·60_0$ | $0·03_7$ | 0·740 | | $3·05_4$ | |
| ×52·31 | 0·752 | | $2·81_3$ | $0·03_8$ | 0·633 | | $3·05_5$ | |
| 63·14 | 0·535 | | $3·08_7$ | $0·03_9$ | 0·483 | | $3·05_7$ | |
| ×74·22 | 0·314 | | $3·43_5$ | $0·03_9$ | 0·297 | | $3·06_1$ | |
| 82·06 | 0·157 | | $3·81_5$ | $0·03_9$ | 0·153 | | $3·07_2$ | |
| 88·20 | 0·034 | | $4·60_7$ | $0·03_9$ | 0·034 | | $[3·15_3]$ | |
| 89·69 | 0·004 | | $5·44_4$ | $0·03_9$ | 0·004 | | $[3·05_8]$ | |
| 89·90* | 0 | 0 | | | | | | |
| 91·78 | | 0·038 | $6·62_0$ | $0·03_9$ | | 0·041 | | $[7·98_9]$ |
| 97·00 | | ×0·142×× | $7·33_8$ | $0·03_9$ | | 0·155 | | $7·97_3$ |
| 109·88 | | 0·400×× | $8·10_7$ | $0·03_8$ | | 0·437 | | $8·21_7$ |
| 125·14 | | ×0·705×× | $8·84_1$ | $0·03_8$ | | 0·769 | | $8·31_9$ |
| 131·75 | | 0·837 | $9·38_6$ | $0·03_7$ | | 0·910 | | $[8·38_1]$ |

* Inflexion point read graphically.

was 131·75 cu. mm., the total change in volume was only from 5 to 5·13 c.c., and may be neglected in the following calculations. No accurate corrections for liquid junction potentials could be made since the mobility of the clupein ion is unknown. In order to give a maximum value for this potential (against 3·5 $N$ KCl) it was calculated by means of Henderson's equation in the form used by Bjerrum and Unmack [4] and assuming that the mobility of the clupein ion is zero (see Table II., column 5). The results are shown in Table II. and Fig. 2.
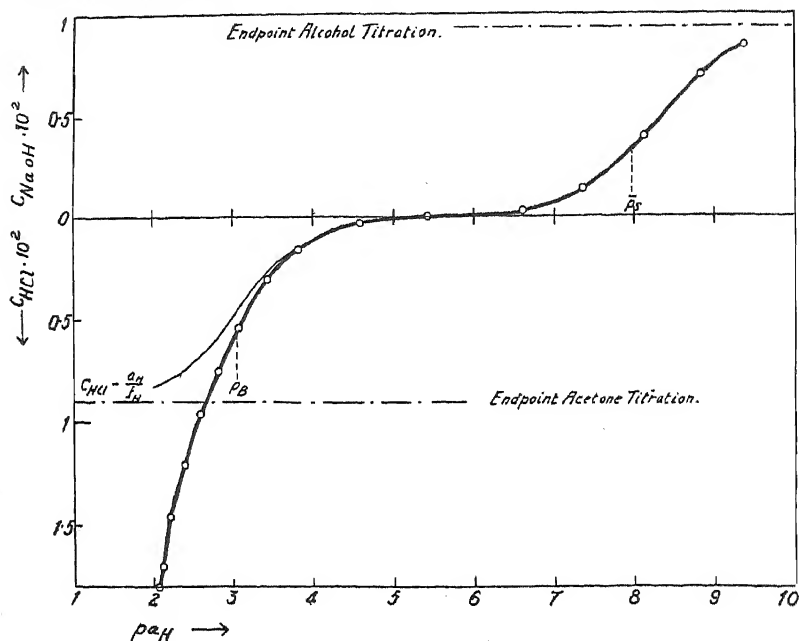


FIG. 2.

From these is seen that the ionisation curve is apparently of a very simple type, and very much like that of the curves for amino-acids and peptides. It has two distinct branches, corresponding to two stages of ionisation, and three inflexion points, of which the one in the middle has a tangent almost parallel with the abscissæ and corresponds to the amphoionic state of the protein.

### 3. Theoretical.

We shall first assume that clupein is a single substance and, on this basis, determine the ionisation constants for the equilibria. The only quantities of this kind we are able to estimate are the incomplete ionisation constants,[4] defined by the equations

$$K_{B}' = \frac{[\text{clup}]a_{H}}{[\text{clup}^+]} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

and

$$K_{S}' = \frac{[\text{clup}^-]a_{H}}{[\text{clup}]} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

in which [clup], [clup $^+$] and [clup $^-$] denote the concentrations of the amphoion and the ions with one more and one less positive charge respectively. $a_{H}$ is the hydrogen ion activity.

In the first expression the amphoion acts as a base, (*i.e.*, takes up hydrogen ions [5] at the carboxyl end) in the second as an acid (*i.e.*, gives of hydrogen ions from the amino end).

Equations (1) and (2) may be written as follows :

$$K_B' = K_B \cdot \frac{f+}{f+-} = \frac{\left[c_T - c_{HCl} + \dfrac{a_H}{f_H}\right]a_H}{c_{HCl} - \dfrac{a_H}{f_H}} \qquad . \qquad . \quad (3)$$

$$K_S' = K_S \cdot \frac{f+-}{f-} = \frac{\left[c_{NaOH} - \dfrac{K_W}{a_H \cdot f_{OH}}\right]a_H}{c_T - c_{NaOH} + \dfrac{K_W}{a_H \cdot f_{OH}}} \qquad . \qquad . \quad (4)$$

where :—

$K_S$ and $K_B$ : True ionisation constants.
$f + -$, $f +$ and $f -$ : Activity coefficients of the amphoion and of the ions with one more and one less positive charge.
$c_T$ : Total concentration of clupein (molarity).
$c_{HCl}$ and $c_{NaOH}$ : Total normality (bound + free) of acid and base respectively, calculated from the original amounts of base used in the titration fixing the inflexion point at $pa_H$ 5·6 as zero point (see Table II.).
$f_H$ and $f_{OH}$ : Activity coefficients of the H and OH ions.
$K_W$ : Dissociation constant of water.

The negative logarithms of the constants, $K_B'$ and $K_S'$, will, hereafter be denoted by $p_B$ and $p_S$.

In order to find their value we may proceed in two different ways, a and b, one of which gives, at the same time, an independent determination of the molecular weight of the clupein.

**a. First Method.**—The accurate figures for the titrations in alcohol and acetone were, reckoned from the inflexion point :

46·45 cu. mm. $N/1$ NaOH and 45·17 cu. mm. $N/1$ HCl per 5 c.c. solution A ; average 45·81 or expressed as equivalents per g. of clupein, 2·423 × 10⁻⁴. Molecular weight of clupein 4130. Molar concentration $c_T$ of clupein in solution A, 0·916 × 10⁻².

Of the other quantities in equations (3) and (4), then, only $f_H$ is left to be determined, since $\dfrac{K_W}{a_H \cdot f_{OH}}$ in our $pa_H$-range is so small that putting $K_W$ equal to 10⁻¹⁴ and $f_{OH}$ equal to $f_H$ is sufficiently accurate. $f_H$ was calculated from the equation :

$$- \log f_H = 0 \cdot 166 \sqrt[3]{c} - 0 \cdot 185 \cdot c - 0 \cdot 003$$

given by Bjerrum and Unmack [4] introducing for $c$ the value * 0·30 $N$.
Hence the value for $f_H$ used was 0·88.

Now the terms

$$x = \frac{c_{HCl} - \dfrac{a_H}{f_H}}{c_T} \qquad . \qquad . \qquad . \qquad . \qquad . \quad (5)$$

and

$$y = \frac{c_{NaOH} - \dfrac{K_W}{a_H \cdot f_{OH}}}{c_T} \qquad . \qquad . \qquad . \qquad . \quad (6)$$

* One of the assumptions underlying this is that the contribution of the clupein ion to the ionic strength is the same as that of a monovalent ion of the twentyfold concentration, *viz.* 0·18 $N$. This is at any rate not very unlikely seen from the following point of view. The smallest distance between any two charges in the clupein ion is of the order of magnitude 7Å whereas the value of $1/\kappa$ (Debye) is < 3Å. Therefore it seems rather improbable that more than one charge of a clupein ion could enter into the ion atmosphere of a hydrogen ion at a time. Another assumption is that specific interaction between the clupein ions and the hydrogen ions is negligible. This may be permitted since in the $pa_H$-range where the term $a_H/f_H$ is of importance there are relatively few negative charges situated on the clupein ions.

may be computed, and from (3) and (4) we obtain

$$p_B = pa_H - \text{Log} \frac{1 - x}{x} \qquad . \qquad . \qquad . \qquad (7)$$

$$p_S = pa_H + \text{Log} \frac{1 - y}{y} \qquad . \qquad . \qquad (8)$$

The quantities $x$ and $y$ are given in Table II together with the values for $p_S$ and $p_B$ calculated from (7) and (8).

The table shows that while $p_B$ is perfectly constant within a broad $p_H$ range, $p_S$ varies considerably. This is no accident as the same phenomenon was found also for other fractions and generally the more pronounced the less pure the fractions happened to be ; so the variation of $p_S$ is undoubtedly due to this clupein fraction 6 being a mixture. The reason why $p_B$ is less affected by this circumstance than is $p_S$ may be found in the fact previously mentioned, that at the carboxyl end of the different clupein chains there is probably always situated an arginine molecule, whereas we know little or nothing about the arrangement of the amino acids in the amino end. This may vary from one clupein component to another, giving rise to such differences between their ionisation constants ($p_S$) as would cause the observed complexity of the ionisation curve of the mixture * (see p. 332).

Apart from this special circumstance considering all investigated amino-acids and peptides together, any mixture of these substances would tend to show the same difference between the behaviours of $p_B$ and $p_S$ because the range of variation of $p_S$ is far broader than that of $p_B$ (see e.g., Cohn [7]).

**b. Second Method.**—Supposing the clupein fraction in question to be a single substance, and $K_B'$ to be constant, by means of (3), $c_T$, $f_H$ and $K_B'$ may be computed from 3 points of the titration curve (marked with crosses in Table II.).

* One more possible, but unlikely, explanation of the variation of $p_S$ may be mentioned. $p_S$ is given by the equation

$$p_S = \text{constant} - \log . \frac{f + -}{f -}.$$

Therefore, if $\frac{f + -}{f -}$ varies with $pa_{H^.}$, $p_S$ will also vary. Now, if $\frac{f + -}{f -}$ is calculated strictly on the basis of the Debye-Hückel theory, its variation with $pa_H$ may be quite considerable. It increases, however, with increasing $pa_H$. thus causing $p_S$ to decrease, contrary to the observation. Moreover—there is reason to believe that the ionic strength is much more constant than might be expected from the results of any direct application of this theory ; and, additional considerations, of the same kind as on given p. 329, tend to show that, in cases where the distances between the charges of an ion I are great compared with $1/\kappa$, the valency of the ion enters only with its first power, and not with its square, into the theoretical constant $A_I$ of the Debye expression

$$- \log . f_I = A_I \sqrt{\mu}$$

(in which $\mu$ is the ionic strength). Making this assumption the variations of $\log . \frac{f + -}{f -}$ may be neglected.

Of course, there may be specific interactions causing $\frac{f + -}{f -}$ to vary. It would, however, then be hard to explain why $\frac{f + -}{f +}$ is a constant, as it actually seems to be. We shall therefore assume that both of these ratios are constant under the given experimental conditions, preferring the simple explanations of the variation of $p_S$ given above.

The values obtained were, compared with those previously found,

| Method. | $c_T \times 10^2$. | $f_H$. | $p_B$ Average. | Molecular Weight. |
|---|---|---|---|---|
| $a$ | 0·916 | 0·88 | 3·06 | 4130 |
| $b$ | 0·900 | 0·87* | 3·07 | 4200 |

* With six other clupein preparations the following $f_H$ values were found 0·86, 0·87, 0·86, 0·91, 0·85, 0·88.

The agreement is excellent.

In case of the alkaline branch, disregarding the term $\dfrac{K_W}{a_H \cdot f_{OH}}$ two points of the titration curve will suffice for a determination of $c_T$ and $p_S$. The following values were obtained :

| Method. | $c_T \times 10^{-2}$. | $p_S$. | Molecular Weight. |
|---|---|---|---|
| $a$ | 0·916 | 7·97-8·32 | 4130 |
| $b$ | 0·808 | 8·02 | 4680 |

The agreement is not so good, which is to be expected. The following rough and quite simple extrapolation method gives better values.

Denoting $\left( c_{NaOH} - \dfrac{K_W}{a_H \cdot f_{OH}} \right)$ by $Z$,

(4) may be written

$$\frac{1}{Z} = \frac{1}{K_S' \cdot c_T} \cdot a_H + \frac{1}{c_T} \qquad . \qquad . \qquad . \qquad . \qquad (9)$$

This is valid for a single substance. The equation represents a straight line when $1/Z$ is plotted against $a_H$. $\dfrac{1}{c_T \cdot K_S}$ is the slope of the line, and $\dfrac{1}{c_T}$ the point where it cuts the $1/Z$-axis.

For a mixture of $n$ components with the concentrations $(c_T)_i$ and ionisation constants $(K_S')_i$ the following expression holds good :

$$\frac{1}{Z} = \frac{1}{\displaystyle\sum_n \frac{(c_T)_i}{\dfrac{a_H}{(K_S')_i} + 1}} \qquad . \qquad . \qquad . \qquad . \qquad (10)$$

This represents a complex curve which, of course, cuts the $1/Z$-axis at the point

$$\left( \frac{1}{Z} \right)_0 = \frac{1}{\displaystyle\sum_n (c_T)_i} \qquad . \qquad . \qquad . \qquad . \qquad (11)$$

From (11) the average molecular weight $\bar{M}$ of the $n$ components may be computed, viz. :

$$\bar{M} = \frac{\displaystyle\sum_n M_i (c_T)_i}{\displaystyle\sum_n (C_T)_i} = \left( \frac{1}{Z} \right)_0 \times \text{(grs. of clupein per litre)} \qquad . \qquad (12)$$

Again, the slope of the curve represented by (10), with increasing $a_H$ approaches the value :

$$S_\infty = \frac{1}{\displaystyle\sum_n (c_{Ti})(K_S')_i} ; \qquad . \qquad . \qquad . \qquad (13)$$

so from (13) the average of $K_S'$, $\bar{K}_S'$, may be calculated :

$$\bar{K}_S' = \frac{\sum\limits_{n} (c_T)_i (K_S')_i}{\sum\limits_{n} (c_T)_i} = \left(\frac{1}{Z}\right)_0 \cdot \frac{1}{S_\infty}.$$

The following results were obtained :

$$\sum (c_T)_i = 0.911 \times 10^{-2} ; \quad \bar{M} = 4150 ; \quad \bar{p}_S = 7.98.$$
$$(\bar{p}_S = -\log \bar{K}_S')$$

$\bar{M}$ is in good agreement with the $M$-value found from the acid branch of the curve.

If we want to know more about the actual values of the $(K_S')_i$ we shall have to make certain assumptions. The number of points at the titration curve, and their accuracy, will determine the fineness with which the curve can be analysed. In the present case an analysis is only possible if we assume that only two different substances ($S'$ and $S''$) are present. Thus from (10) we obtain

Substance $S'$    $c_T' = 0.270 \times 10^{-2}$    $p_S' = 7.58$
     ,,      $S''$    $c_T'' = 0.641 \times 10^{-2}$    $p_S'' = 8.48.$

The calculation was carried out from the 3 values marked $\times\times$ in Table II.* For the two residual points the $Z$-values shown in Table III. were calculated.

The calculated $\bar{p}_S$-value was 7.996 against the one found by extrapolation, 7.98.

This rather elaborate discussion is given in order to secure the not unimportant result previously outlined that giving the clupein in question a molecular weight of around 4150 it will contain 1 free

**TABLE III.**

| $pa_H.$ | $Z$ Found [See Table II.). | $Z$ Calc. |
|---|---|---|
| 6.620 | 0.038 | 0.036 |
| 9.386 | 0.834 | 0.837 |

carboxyl group and 1 free amino or imino group per molecule, and that, on the basis of our knowledge of the structure of this protein, these groups can only be the ones situated at the ends of the open peptide chain, one of them thus being an $\alpha$-amino or an $\alpha$-imino group. The molecular weight determined in this way is only an average, and it is, of course, impossible on the present basis to estimate the individual molecular weights of the simple components—such as $S'$ and $S''$. As, however, the molecular weights of a crude preparation, and of six fractions prepared from such a one, without significant losses in material, had the following values (determined in the above given way) 4090, 4130, 4110, 3990, 4180, 3870 † and 3550,† one seems justified in assuming that, although the species of amino-acids by which the chains are built up, may vary from one component to another, the chain length is fairly constant.

* For the sake of completeness it may be mentioned that the alkaline branch of the curve on Fig. 2 *cannot* come into existence by superposition of the ionisation curves of two different groups situated in *the same* molecule of clupein. The curve would, in this case, either be a simple ionisation curve, or we should have to assume that $c_T$ was half the above calculated value ($0.9 \times 10^{-2}$). This would, however, involve also that two carboxyl groups were situated on one clupein molecule, which again would make an explanation of the acid branch impossible. Further —even disregarding this fact—no adjustment of the theoretical curve for the alkaline region to the experimental one is possible on this basis.

† These were of the least pure fractions.

## C. Further Conclusions.

In the preceding paragraph some qualitative considerations of the interionic forces in solutions of clupein chloride were given. There is hardly any doubt that they will hold good with sufficient approximation, in cases where we are only concerned with the variation of quantities such as $f_H$ and $\frac{f+-}{f+}$ or $\frac{f+-}{f-}$, caused by small changes in the condition of the solution during titration. The idea that an $n$-valent ion, with long distances between its charges, will behave like a monovalent ion with the $n$-fold concentration is by no means new (compare [24], [25], [26], [28]), although it is as yet not strictly proven.[1], [15], [18]

It is quite another matter, however, if we wish strictly to compare our results with those obtained for the amino acids or for other peptides. Then the absolute magnitude of the ratios $\frac{f+-}{f+}$ and $\frac{f+-}{f-}$ must be determined under the given conditions. That such a determination presents very great theoretical difficulties, even in case of simple amino acids, is well known, and we shall, therefore, have to content ourselves with the rather uncertain comparison of the incomplete ionization constants of clupein with the corresponding quantities of the amino acids and peptides. Then the comparison may or may not give some information about the justification of this procedure.

From the rather spare material (see Cohn [7]) of peptides investigated, it appears that $p_S$ and $p_B$ for peptides build up of simple amino acids, such as glycine and alanine, with increasing chain length approach the values

$$p_S = 7 \cdot 9, \quad p_B = 3 \cdot 3.$$

Introducing, into a chain of 28 amino acids of this kind, 20 charges, distributed in the way shown on Fig. 1, would bring about a diminution $\delta$ of these quantities determined by the expression (see e.g., Bjerrum [9])

$$\delta = \log e^{\Sigma \frac{\varepsilon^2}{DKTa_i}} = 2 \cdot 9 \sum \frac{1}{a_i}$$

in which the $a_i$'s (expressed in Å.) are the distances from the group in question to the different charges. This expression is valid only at infinite dilution, and takes account only of the purely ionic effect, and not of any other changes in $p_S$ and $p_B$ caused by the substitution. At finite ion concentrations it may be corrected by means of the factors $e^{-\kappa a_i}$ (see [8]) in which $\kappa$ has the value $0 \cdot 10$ if $a_i$ is expressed in Å. and the ionic strength is taken to be $0 \cdot 1$, i.e., disregarding the share of the clupein chloride in this. So we have

$$\delta = 2 \cdot 9 \sum \frac{1}{a_i} \cdot e^{-0 \cdot 1 a_i}.$$

In our case we then get approximately :

$$(\delta)_{p_S} = 0 \cdot 34 \quad \text{and} \quad (\delta)_{p_B} = 0 \cdot 46$$

or

$$(p_S)_{corr.} = 7 \cdot 56 \quad \text{and} \quad (p_B)_{corr.} = 2 \cdot 84.$$

Considering the suppositions, and the lack of knowledge of the true arrangement of the arginines in the chain, these values agree rather well with those found taking the substance $S'$ (see p. 332) as a type. The ionisation constant of substance $S''$ corresponding to $p_S$ equal to $8 \cdot 48$ is, however, far too low ; so we shall have to assume either a specific structure of this substance or that hydroxy proline is situated at the

" amino " end. This imino acid is the only one (compare [7]) which is so weak an acid ($p_S$ = 10·6 against 9·7 for glycine) that the high $p_S$-value of $S''$ could be explained in the above way.

In this connection it is of interest to mention that the ratio of free $\alpha$-amino nitrogen (after van Slyke), to free $\alpha$-imino + $\alpha$-amino nitrogen (alcohol titration) is about 0·3 for the clupein fraction investigated. This is identical with the ratio $\dfrac{c_8{'}}{c_8{'} + c_8{''}} = 0\cdot296$. Unfortunately the van Slyke method is not very reliable in this case because of the high content of arginine in clupein, its guanido group reacting slowly with $HNO_2$. The value is the one after 5 min. shaking and during this time, according to Plimmer [21] hardly significant amounts of $N_2$ are liberated from the guanido groups. The matter is being investigated further.

Finally, a few words must be said about the ionisation of arginine. The guanido group is known to be a strong base and the charged group, therefore, a correspondingly extremely weak acid, having its $p_S$ at about 12·5. If we now assume that all the twenty charged guanido groups in the clupein molecule have about the same de-ionisation " tendency " then, for pure statistical reasons (Adams [2]) the first step of de-ionisation will have its $p_S$ at $pa_H$ = 12·5 — log 20 = 11·2. To this comes the repulsion effect from the other charges giving again a diminution of about 0·3. These two factors alone therefore bring the $p_S$ down to 10·9, no other substitutional effects as yet having been accounted for. From a paper by Greenstein [11] it appears also that these effects (in lysine peptides, it is true) tend to push $p_S$ in the same direction. It is, therefore, surprising that the guanido groups do not disturb our titrations, but it is, of course, impossible to draw any certain conclusions. Other electrometric titrations of other fractions of clupein have been carried considerably further to the alkaline side than the one described in this paper, and the results show that the de-ionisation of the charged guanido group hardly *begins* until $pa_H$ 9·5 — 10 is reached. The specific structure of the clupein chain may thus have an unexpected weakening effect upon the acidity of the charged guanido groups.

The possibility of the peptide bonds taking part in the ionisation processes is hardly to be considered. Unfortunately the interesting results found by Stiasny and Scotti [27] with glycine peptides are given in a form that does not allow the reader to make any calculations. Possibly these peptides, which also react abnormally with $HNO_2$, represent a special case.

REFERENCES.

[1] Adair, G. S., *Proc. Roy. Soc.*, **120A**, 573, 1928.
[2] Adams, E. Q., *J. Amer. Chem. Soc.*, **38**, 1503, 1916.
[3] Bjerrum, N., *Z. physikal. Chem.*, **106**, 219, 1923.
[4] Bjerrum, N., and Unmack, A., *Det kgl. danske Vidensk. Selsk. Mat.-fys. Medd.*, **9**, No. 1, ·1929.
[5] Brønsted, J. N., *Chemical Reviews*, **5**, 231, 1925.
[6] Cohn, E. J., *Physiol. Rev.*, **5**, 249, 1925.
[7] Cohn, E. J., *Ergeb. Physiol.*, **33**, 781, 1931.
[8] Debye, P., *Physik. Z.*, **24**, 185, 1923.
[9] Felix, K. and Dirr, K., *Z. physiol. Chem.*, **184**, 111, 1929.
[10] Foreman, F. W., *Biochem. J.*, **14**, 451, 1920.
[11] Greenstein, J., *J. biol. Chem.*, **101**, 603, 1933.
[12] Hammarsten, E. and H., *Medd. Kgl. Vetensk. Acad.*, 8, No. 27, 1923 ; Hammarsten, H., *Biochem Z.*, **147**, 481, 1924.
[13] Harris, J. L., *Proc. Roy. Soc.*, **95B**, 440, 500, 1923-24.
[14] Kossel, A., *Protamine und Histone*, Leipzig und Wien :.Franz Deuticke, 1929.
[15] Linderstrøm-Lang, K., *Compt.-rend. Lab. Carlsberg*, **15**, No. 7, 1924.

[16] Linderstrøm-Lang, K., and Lund, E., *Compt.-rend. Lab. Carlsberg*, **16** No. 5, 1926.

[17] Linderstrøm-Lang, K., *Compt-rend. Lab. Carlsberg*, **16**, No. 6, 1926.

[18] Linderstrøm-Lang, K., *Compt.-rend. Lab. Carlsberg*, **17**, No. 4, 1927 ; *Z. physiol. Chem.*, **173**, 32, 1928.

[19] Linderstrøm-Lang, K., and Holter, H., *Compt.-rend. Lab. Carlsberg*, **19**, No. 4, 1931 ; *Z. physiol. Chem.*, **201**, 9, 1931.

[20] Linderstrøm-Lang, K., *Ergeb. Physiol.*, **35**, 415, 1933.

[21] Plimmer, R. H. A., *Biochem. J.*, **18**, 105, 1924.

[22] Rasmussen, K. E., *Compt.-rend. Lab. Carlsberg*, **20**, No. 6, 1934 ; *Z. physiol. Chem.*, **224**, 97, 1934.

[23] Rasmussen, K. E., and Linderstrøm-Lang, K., *Z. physiol. Chem. and Compt. rend. Lab. Carlsberg, in press*, 1934.

[24] Simms, H. S., *J. Gen. Physiol.*, **11**, 629, 1928 ; **12**, 231, 1928 ; **14**, 87, 1930.

[25] Stadie, W. C., *J. biol. Chem.*, **77**, 70, 1928.

[26] Stadie, W. C., and Sundermann, F. W., *J. biol. Chem.*, **91**, 227, 1931.

[27] Stiasny, F., and Scotti, H., *Ber.*, **63**, 2977, 1930.

[28] van Slyke, D. D., Hastings, A. B., Murray, C. D., and Sendroy, J., *J. biol. Chem.*, **65**, 701, 1925.

[29] Waldschmidt-Leitz, E., Ziegler, F., Schäffner, A., and Weil, L., *Z. physiol. Chem.*, **197**, 219, 1931.

[30] Willstätter, R., and Waldschmidt-Leitz, E., *Ber.*, **54**, 2988, 1921.

# THE REACTION BETWEEN GELATIN AND ELECTROLYTES IN GELATIN GELS.

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Many observations have been made on the distribution of electrolytes between two phases in equilibrium, such as a protein *sol* and a salt solution separated by a semipermeable membrane, but similar investigations concerning a protein *gel* exchanging ions with a solution are not numerous. On the occasion of the general discussion held by the Faraday Society in 1930 on Colloid Science applied to Biology, I presented some observations on this subject. They concerned two distinct points of investigation : 1°. What type of reaction is there between the protein and electrolytes when it takes place in conditions where the protein is in the gel state ? 2°. When a swollen gel is in equilibrium of diffusion with a solution of electrolytes, are the ions evenly distributed in all parts of the gel or not ? I present now a few more observations on these two aspects of the study of the chemical properties of gels.

## 1. Chemical Reactions between Inorganic Electrolytes and Gelatin in the Gel State.

In 1930, I studied the case of blocks of gelatin gels immersed in calcium chloride solutions at various $p_H$ values between $p_H$ 3 and 7, and came to the conclusion that only the acid carboxyl and basic amino groups at the surface of the micelles reacted with the diffusing ions ; that there was no evidence of surface adsorption and that at $p_H$ 4·8 there was no reaction at all between the protein and the electrolytes. It seemed interesting to examine the situation in the case of other electrolytes, and I present now my results with sodium chloride and magnesium sulphate.

## Sodium Chloride.

Gels of 7 to 8 per cent. were prepared with isoelectric gelatin,[1] and divided into blocks of about 1 to 2 c.c. ; sometimes they were prepared with the salt solution, sometimes not.   They were immersed in dilute NaCl solutions, containing some acid in Experiment No. 1, a buffer mixture of acetic acid-sodium acetate of $p_H$ 4·8 in Experiment No. II, and nothing else but NaCl in Experiment No. III.   The total volume of the blocks of gel was about 100 c.c., that of the solution, from 500 to 800 c.c.   The temperature was kept constant, below 20° C.   The $p_H$ of the solution was measured every day and it reached a constant value after about five days.   The blocks were then separated from the solution, wiped with ash-free filter paper, divided into three groups for determination of the total volume of gel in each group.[2]  ·The three groups, as well as a sample of the solution were evaporated to dryness after neutralisation with $CaCO_3$, ignited at a temperature not exceeding 400° C., in an electric oven, and analysed for sodium (Barber and Kolthoff's gravimetric method, uranyl-zinc-sodium acetate) and chlorine (micro-Volhardt's method). The results are given in milliequivalents per litre. In the gel, the space occupied by the protein is disregarded, the concentrations of ions being thus calculated for the total amount of water in the gel and not the total volume of gel.   This calculation is only an approximate one, but sufficiently accurate however for the purpose ; the evaluation was based simply on the amount of gelatin in gm. per unit volume of gelatin and not on specific volume of gelatin.   The data given in Table I. show that Donnan's equilibrium equation holds quite satisfactorily although analytical concentrations were used instead of activities.   It seems as if the activities of both $Na^+$ and $Cl^-$ ions were not very appreciably altered in the gel, at the low concentrations used.   Perhaps there is a slight exception in this respect at the isoelectric point (Exp. II) because of the slight disagreement in the results here.

My observations with NaCl are the same as those which I published in 1930 for $CaCl_2$.[3]   More recently, similar experiments were made in dialysers with gelatin *sols* and calcium acetate,[4] and these led to the conclusion that some unionised calcium was bound, not coming into account in Donnan's membrane equilibrium equation.   In these experiments, the conditions allowed more accurate determinations than in mine with gels.   Anyhow, the amounts of unionised calcium bound to gelatin, expressed in millimoles of Ca per gm. of protein are very small and do not alter very appreciably my previous observations with $CaCl_2$. The fact that in the latter, the ion product in Donnan's equation was always very slightly higher for the gel than for the solution is perhaps an indication that a very small part of calcium was eventually bound and unionised and should not have come into account in the equation. But the same fact may also be attributed to small deviations of activity coefficients of the ions in the gel.

From my observations with NaCl it seems also that in gelatin gels, practically all the water present has not lost its ordinary solvent properties.   I came to the same conclusion in 1930 with $CaCl_2$.   This seems in agreement with many other recent observations on bound water in protein sols.[4, 5]

[1] Isoelectric gelatin was prepared according to J. H. Northrop's and M Kunitz's method [*J. gen. physiol.*, **11**, 477, 1927-28).
[2] This was done in measuring flasks of the type indicated in Fig. 1B.
[3] *Trans. Faraday Soc.*, **26**, 717, 1930.
[4] W. G. Eversole, L. A. Ford and G. W. Thomas, *J. Biol. Chem.*, **104**, 107, 1934 ; D. M. Greenberg, *ibid.*, **105**, 511, 1934 ; and W. G. Eversole, *ibid.*, **105**, 515, 1934.
[5] D. M. Greenberg and M. M. Greenberg, *J. gen. physiol.*, **16** *ssq.*, 1933.

Now let us consider the type of reaction taking place between the protein and the electrolytes in the gel. The situation may be pictured in two different manners, as indicated on Table II. The upper part of the table (compartments 1 to 4) shows what relations one should find in case of reactions due to electrolytic dissociation of the organic acid or basic radicals of the protein at the surface of the micelles, whereas the lower part of the table shows what the situation would be if adsorption of the penetrating acids or bases took place at the same surface (compartments I to IV).

TABLE I.—NaCl.

| | | Blocks. | Solution. |
|---|---|---|---|
| *Exp. No. I.*<br>**Initial State.** Solution, $p_H$ 2 ($H_2SO_4N/_{100}$), NaCl $N/_{50}$; gel, 7 per cent. gelatin, NaCl $N/_{50}$. | Cl⁻ | $\left.\begin{array}{l}19\cdot1\\18\cdot9\\20\cdot1\end{array}\right\}\begin{array}{l}19\cdot4\\:0\cdot97\end{array}=$<br>$19\cdot9$ | **17·8** |
| **At Equilibrium.** Solution, $p_H$ 3·2; gel, 2·7 per cent. gelatin<br>$(Na^+)_1 \times (Cl^-)_1 = (Na^+)_2 \times (Cl^-)_2$<br>$19\cdot9 \times 19\cdot4 = 17\cdot8 \times 22\cdot4$<br>$386 \qquad\qquad 398$<br>average value $= 392$ ($\pm 1\cdot5$ per cent.). | Na⁺ | $\left.\begin{array}{l}18\cdot9\\19\cdot1\\18\cdot6\end{array}\right\}\begin{array}{l}18\cdot9\\:0\cdot97\end{array}=$<br>$19\cdot4$ | **22·4** |
| *Exp. No. II.*<br>**Initial State.** Solution, $p_H$ 4·9 to 5·0, NaCl $N/_{100}$, buffer mixture, $N/_{100}$; gel, 7 per cent. gelatin, NaCl $N/_{100}$ and same buffer mixture. | Cl⁻ | $\left.\begin{array}{l}10\cdot6\\10\cdot7\\10\cdot7\end{array}\right\}\begin{array}{l}10\cdot7\\:0\cdot94\end{array}=$<br>$11\cdot4$ | **10·3** |
| **At Equilibrium.** Solution, $p_H$ 4·9; gel, 5·8 per cent. gelatin.<br>Equation at equilibrium :<br>$11\cdot4 \times 26\cdot6 = 10\cdot3 \times 25\cdot5$<br>$303 \qquad\qquad 263$<br>average value, $283$ ($\pm 6\cdot6$ per cent.) | Na⁺ | $\left.\begin{array}{l}24\cdot8\\25\cdot1\\25\cdot1\end{array}\right\}\begin{array}{l}25\cdot0\\:0\cdot94\end{array}=$<br>$26\cdot6$ | **25·5** |
| *Exp. No. III.*<br>**Initial State.** Solution neutral, NaCl $N/_{50}$; gel, 7 per cent. gelatin, NaCl $N/_{50}$. | Cl⁻ | $\left.\begin{array}{l}17\cdot5\\17\cdot2\\17\cdot7\end{array}\right\}\begin{array}{l}17\cdot46\\:0\cdot96\end{array}=$<br>$18\cdot2$ | **20·9** |
| **At Equilibrium.** Solution, $p_H$ 5·9; gel, 4 per cent. gelatin.<br>Equation at equilibrium :<br>$18\cdot2 \times 23\cdot9 = 20\cdot9 \times 21\cdot0$<br>$434 \qquad\qquad 440$<br>average value, $437$ ($\pm 0\cdot8$ per cent.) | Na⁺ | $\left.\begin{array}{l}22\cdot7\\23\cdot0\\23\cdot0\end{array}\right\}\begin{array}{l}22\cdot9\\:0\cdot96\end{array}=$<br>$23\cdot9$ | **21·0** |

Let us consider four different cases : (1) $p_H$ more acid than that corresponding to the isoelectric point ; (2) the isoelectric point ; (3) $p_H$ slightly acid between the isoelectric point and the neutrality ; (4) alkaline solutions. In the first and last cases, surface ionisation or surface adsorption of acids or bases will lead qualitatively to the same situation (compare 1 with I, and 4 with IV) ; in both eventualities the predicted relations are those which are found by experience and it is not possible

to choose.   Perhaps both reactions take place simultaneously.   But
if we consider now the two intermediate cases 2, II and 3, III, the re-
lations are qualitatively different.   In case of surface adsorption of an
acid the relation should be, in II and in III, of the same type as that in I
but simply less pronounced.   In case of surface ionisation the situation
is different (compartments 2 and 3).   By experience, one finds that
the relations are those which correspond to compartments 2 and 3,
and not II and III.   In other words, were we dealing with surface ad-
sorption, the isoelectric point should be found in neutral solution only.
It seems, therefore, that in slightly acid, neutral, or slightly alkaline
solutions, say between approximately $p_H$ 3 and 8, the surface ionisation
of the protein is the predominant factor of its chemical reactions with
other ions, in the gel state.   It is possible that in more strongly acid
or alkaline solutions, another factor, namely surface adsorption of acids

TABLE II.



or bases also comes into account in addition to the first one.   In bio-
logical conditions therefore, the first factor seems to be the chief de-
termining one, practically the only one.   It is known that the maximum
base capacity of gelatin corresponds to about 0·7 milliequivalents per
gm. of gelatin.[6]   This covers very largely the difference of concentration
found for Na in Exp. III, Table I.

Another type of surface adsorption might also be considered, namely
the adsorption of the neutral salt itself rather than acids or bases.   For
example :

$$[(\mathbf{P})Cl]^- \; Na^+ \atop Cl^- \; Na^+ \Big| \; Na^+ \; Cl^-$$
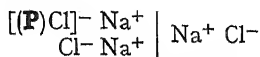
This however is, in no instance, the case for sodium chloride, because
then, part only of the ions and not its total amount found in ash, should
have to come into account in Donnan's equilibrium equation.

[6] Rawlins and Schmidt, *J. biolog. Chem.*, **82**, 709, 1929.

The experiments with sodium chloride confirm those previously published for calcium chloride. But we shall see now that the same situation cannot be generalised to all electrolytes. This will become apparent from what is found in the case of magnesium sulphate.

## Magnesium Sulphate.

Exactly the same type of experiment as that described for NaCl has been repeated with magnesium sulphate and the results are given on Table III.[7] In Exp. No. I, on the acid side of the isoelectric point, there is the same type of relation as the one found for NaCl or $CaCl_2$

TABLE III.—$MgSO_4$.

|  |  | Blocks. | Solution. |
|---|---|---|---|
| *Exp. No. I.*<br>**Initial State.** Solution, $p_H$ 2 ($H_2SO_4$ $N/_{100}$), $MgSO_4$ $N/_{20}$; gel, 7 per cent. gelatin, $MgSO_4$ $N/_{20}$. | S. | $\left.\begin{array}{l}62\cdot1\\62\cdot5\\62\cdot3\end{array}\right\}\begin{array}{l}62\cdot3\\:0\cdot98=\\63\cdot6\end{array}$ | **54·1** |
| **At Equilibrium.** Solution, $p_H$ 3·4 (gelatin about 0·5 per cent.); gel, 2·5 per cent. gelatin. |  |  |  |
| **Equation at Equilibrium.**<br>$63\cdot6 \times 49\cdot2 = 54\cdot1 \times 53\cdot8$<br>3129        2910<br>average value, 3019 ($\pm$ 3·7 per cent.). | Mg. | $\left.\begin{array}{l}48\cdot3\\48\cdot3\\48\cdot0\end{array}\right\}\begin{array}{l}48\cdot2\\:0\cdot98=\\49\cdot2\end{array}$ | **53·8** |
| *Exp. No. II.*<br>**Initial State.** Solution, $p_H$ 4·8, buffer mixture $N/_{100}$, $MgSO_4$ $N/_{20}$; gel, 6·8 per cent. gelatin + same buffer mixture + $MgSO_4$ $N/_{20}$. | S. | $\left.\begin{array}{l}54\cdot2\\58\cdot1\\57\cdot3\end{array}\right\}\begin{array}{l}56\cdot5\\:0\cdot95=\\59\cdot5\end{array}$ | **49·0** |
| **At Equilibrium.** Solution, $p_H$ 4·5 − 4·6; gel, 4·9 gm. per cent. gelatin. | Mg. | $\left.\begin{array}{l}52\cdot0\\51\cdot1\\52\cdot6\end{array}\right\}\begin{array}{l}51\cdot9\\:0\cdot95=\\54\cdot6\end{array}$ | **50·2** |
| *Exp. No. III.*<br>**Initial State.** Solution neutral ($MgSO_4$ $N/_{40}$, $p_H$ 5·5 adjusted at $p_H$ 7 with NaOH); gel, 7 per cent. gelatin only. | S. | $\left.\begin{array}{l}29\cdot9\\27\cdot6\\28\cdot1\end{array}\right\}\begin{array}{l}28\cdot5\\:0\cdot96=\\29\cdot7\end{array}$ | **22·4** |
| **At Equilibrium.** Solution, $p_H$ 5·6; gel, 4·4 per cent. gelatin. | Mg. | $\left.\begin{array}{l}25\cdot0\\24\cdot1\\24\cdot8\end{array}\right\}\begin{array}{l}24\cdot6\\:0\cdot96=\\25\cdot6\end{array}$ | **19·0** |

and Donnan's equilibrium equation holds fairly satisfactorily. But at the isoelectric point (Exp. No. II) and at $p_H$ between 4·7 and 7·0 (Exp. No. III), the equation does not hold any more. If we compare the results with the scheme of Table II. (compartments 2, II and 3, III) it

[7] The gels and solution were neutralised with pure $CO_3K_2$ instead of $CO_3Ca$, evaporated to dry residue, ignited according to Stolte's method. Sulphates were determined with Fiske's Benzidine titration method and magnesium with Tisdall and Kramer's titration method.

is easy to see that neither simple surface ionisation of the gelatin micelles nor simple surface adsorption of acid will explain the situation. There is more magnesium and particularly more sulphur in the gel than in the solution, in both cases. Whether this may be explained by the mere fact that activities of $Mg^{++}$ and $SO_4 =$ ions are strongly influenced by the gelatin in the gel, and in that case there is not necessarily an exception to the rule observed for NaCl and $CaCl_2$, or whether there is some non-ionised, still undetermined, complex compound formed, it is actually difficult to tell. Further observations with more dilute solutions of $MgSO_4$ and also with other sulphates will give us perhaps an answer to the question. The question arises also whether some type of surface adsorption of magnesium sulphate takes place in addition to the ordinary and more usual relations.

## 2. Uneven Distribution of Ions in Gelatin Gels.

In 1930, I reported on observations which led me to the conclusion that when a piece of swollen gel is in equilibrium of diffusion with a solution of electrolytes, there is an uneven distribution of the ions which have penetrated in the gel, a concentration gradient of these ions which is probably due to the fact that the superficial concentric layers of the gel swell first aud prevent the inner layers from swelling to the same extent. If this manner of representing the situation in a gel is correct, it is clear that all the data discussed in the first part of this report concern average concentrations in a block of gel.

The observations of 1930 leading to the conception of a gradient distribution of the ions, concerned the diffusion of a base at very low concentration (NaOH about $N/10,000$) in columns of gelatin gels of 7 to 8 per cent. gelatin, kept in test tubes, the solution and gel containing phenol red. The superficial part of the gel became red, the centre staying yellow. After a certain time, the level of gradual change of colour kept itself at a constant depth from the surface for a very long time. These experiments have been criticised for the following reasons : 1°. Electrolytic impurities in the non-purified gelatin I used, may have produced an apparently steady state.[8]  2°. The concentration of the diffusing ion being so small, the case may be an extreme one of very slow diffusion rather than a true steady state.[8, 9]  In order to be able to demonstrate the existence of a concentration gradient it is absolutely necessary to work at concentrations of the penetrating electrolytes which are very small in comparison with the concentration of the protein, in order to obtain a maximum Donnan effect for small differences of concentration of protein. With $0.01N$ acid solutions used by Halpern, and $0.3N$ acid solutions used by Krishnamurti,[10] I quite agree that it is impossible to notice anything else but the ordinary law of physical diffusion. The reason why I keep on working with very dilute NaOH solutions is only imposed by the choice of a suitable indicator with an easily distinguishable colour change at a proper $p_H$ value.

I have repeated therefore my experiments with flowing solutions of sodium hydroxyde at $p_H$ between 9 and 10·5, protected from contamination with $CO_2$ of the air.[11]  The gels were prepared with isoelectric gelatin,

[8] L. Halpern, *J. gen. physiol.*, **14**, 575, 1931.
[9] See also T. R. Bolam, *Kolloid. Beih.*, **39**, 139, 1934.
[10] *Proc. Roy. Soc.*, **122A**, 1929.
[11] This protection was assured as thoroughly as possible but it is hardly possible to prevent it altogether. The solution used here was prepared from a 40 per

the ash content of which was reduced to less than 0·07 per cent. The apparatus used is indicated on Fig. 1A. The gels were used in the form of cubes which were allowed to swell freely. They were supported on a piece of platinum gauze, and a level of mercury could be brought down and up again, in order to allow the gel to emerge occasionally from the dark red solution, for momentary examination during the long period of diffusion, without opening the apparatus. The whole system was held at constant temperature, between o and 5° C., in a cold thermostatic room. Each experiment lasted from one to three months. When the experiment was stopped, a slice of the gel passing through the centre of the block was cut out of the latter for examination. The concentration of the gelatin in the gel, when prepared, was 7 to 8 per cent. After about one month this was brought down to an average value of about 3 per cent. due to swelling. *One never obtains uniform distribution of the colour of the indicator;* even after three and a quarter months (longest period of observation) the nucleus is yellow and the cortex is red, with a gradual change of colour between the surface and the centre, the solution being also red but much darker and purple. After longer periods than three months, the gels tend to fall to pieces and the yellow nucleus becomes colourless; that this has not become alkaline like the cortex can be veri-



FIG. 1.

fied by spreading a drop of fresh indicator solution on the slice of gel. The difference of colour between the nucleus and the cortex develops distinctly This steady state lasting more than ten weeks is schematically represented on Fig. 2 (cubes 6 to 9) ; the dotted part of the cubes corresponds to a red tinge, the clear part to a yellow colour. During this period of one to three months, the size of the cubes corresponded to 30 to 50 mm. length of their side from one experiment to another. The depth of penetration of the $OH^-$ ions in sufficient amount to produce a change of colour from yellow to red was from 6 to 10 mm. according to the case. In order to have an idea of the rate of simple physical diffusion of the base in a gel, at such low temperature and concentration, similar tests were done in blocks of same size made of 5 per cent. agar gels. The rate of migration can be easily followed ; here there is a sharp boundary between the yellow and red parts of the gel as diffusion proceeds. Within four days the slice of
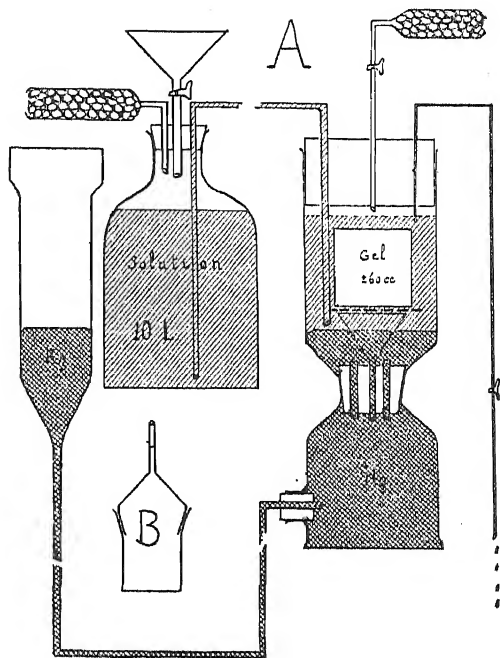
cent. stock solution $CO_2$ free, but when diluted to $0·5 \times 10^{-3}$, some inevitable contamination with $CO_2$ even slight is sufficient to shift the $p_H$ of the solution down between 9 and 10. This was really the $p_H$ of the NaOH solution used in these experiments, although it is indicated as $p_H$ 10·7, theoretical value by titration of the stock after dilution ($0·5 \times 10^{-3}$ $N$).

gel passing through the centre of the block is uniformly red (Fig. 2. Cubes 1 to 4). The rate of diffusion is thus a rapid one. Even if the agar gel contains an acid (we have used lactic acid) at a concentration about 100 times greater than that of the diffusing base, the penetration of the base is still comparatively a rapid one. Acid first diffuses out of the gel, of course, and is neutralised by the slowly flowing solution of dilute NaOH, outside. After two days the concentrations are approximately equalised and the red colour begins to penetrate into the gel ; about six days later, the entire block has become uniformly red (Fig. 2. Cube 5).

Agar. 5 °/₀. $t°$ 0 to 5° C.

24 h.     48 h.     3 days.     4 days.     10 days.

Gelatin 5 °/₀ (3 to 6). $t°$ 0 to 5° C.

1 mth.     1½ mths.     2½ mths.     3½ mths.
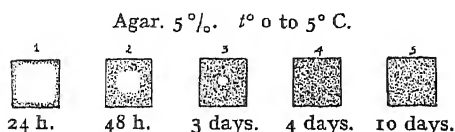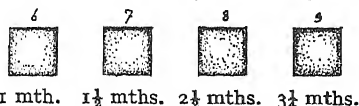
Solution = NaOH $0.5 \times 10^{-3} N$. $p_H$ 10·7.

FIG. 2.

Stiles and other workers have also shown a few years ago that the presence of ions in the gel, capable of forming insoluble salts with the penetrating ion does not retard very considerably the rate of diffusion of the latter in the gel.[12] These observations render it very probable that if simple physical diffusion took place exclusively in the gelatin gel, the colour of the indicator in the gel should be uniformly red within about ten days in the conditions of concentration and of temperature in which these experiments were conducted. It seems, therefore, that the very long-standing gradient concentration observed in the small blocks of gelatin gel during several months can only be explained by a membrane equilibrium with a concentration gradient of the free ions in the gel due to a concentration gradient of the protein structure due

TABLE IV.

|  | $p_H$ of the Melted and Diluted Gel.* | Average Gelatin Concentration in the Undiluted Gel. |
|---|---|---|
| Initial state before diffusion | 5·2 * | 7 gm. per cent. |
| After one month's immersion in nucleus NAOH flowing solution of $p_H$ from 9 to 10         cortex | 5·7 *  7·1 * | 3·9  ,,  ,,   2·8  ,,  ,, |

in turn to uneven swelling of the different parts of the gel. Since this uneven swelling is considered as the determining factor of the gradient effect, I have endeavoured to establish it by direct determinations of the average gelatin concentration in the cortex and in the nucleus of a swollen block of gel.

After one month's immersion of a 7 per cent. block of gelatin gel in dilute NaOH solution of $p_H$ about 9 to 10, its volume has become approximately constant. Then the yellow centre was enucleated,

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[12] *Biochem. J.*, 14, 58, 1920 ; 15, 620 and 629, 1921.

* These $p_H$ values are not those which existed in the gel before it was enucleated and melted. The fact of melting it in some water has probably liberated a few acid valencies. These values simply indicate a *difference* of $p_H$ in different parts of the swollen gel in relation with the fact that sodium hydroxyde has penetrated in *all* parts of the gel but not to the same degree.

the red cortex and the nucleus we separated, weighed, melted in a minimum amount of water, brought to a known volume as small as possible and analysed for nitrogen concentration and $p_H$ (glass electrode). A similar treatment was made in parallel with a freshly prepared gelatin gel which had not been immersed in the alkaline solution ; the results are given in Table IV. After one month's immersion in very slightly alkaline solution, the average gelatin concentration in the cortex is thus but 70 per cent. of what it is in the nucleus ; here the penetration of the solution was, however, sufficient to reduce its original concentration in gelatin to less than one half.

In the experiment here discussed of the penetration of NaOH at low concentration in a gelatin gel, is it theoretically possible that at equilibrium, part of the gel, namely the nucleus can remain yellow to phenol red ? Let us simplify the case and discard the concentration gradient. The situation would be the following :

| Gel. | Solution. |
|---|---|
| $P^-$ Na$^+$ | Na$^+$ OH$^-$ |
| $z$ | $x$ |
| Na$^+$ OH$^-$ | |
| $y$ | |

According to Greenberg and Schmidt's titration curves, the molecular weight of gelatin reduced to one acid valence is about 1700 to 1800.[13] Let us make it roughly 2000 and assume that this still holds approximately in the gel state ; $z$ is thus about $10^{-2}$ $N$ in 2 to 5 gm. per cent. gelatin gels. $x$ lies between $10^{-4}$ and $10^{-5}$ $N$ (see note [11]). $z$ is thus at least 100 times greater than $x$. $y$ will be at least 100 times smaller than $x$ [14] ; hence, the $p_H$ in the gel will lie between 7 and 8, exactly the range of maximum change of colour of phenol red. As a matter of fact, gels containing this indicator will never become red even near the surface, when immersed in very slightly less alkaline solution than the one used here ; whereas very slightly more concentrated solutions will produce a uniform red colour throughout all parts of the gel in a fairly short time.

The question of establishing directly, experimentally, the existence of a long-standing concentration gradient in a block of swollen gel being a very important point in the phenomenon here described, I wished in conclusion, to examine again this point in the case of pronounced swelling in relatively strong acid solution. Several blocks of gel were immersed in a large excess of 0·01 $N$ solution of strong acid at 0 to 5° C. A block was picked out every week, enucleated and the average concentration of gelatin determined in the nucleus and in the cortex. Similar blocks which were not immersed in the acid solution were also analysed immediately after they were prepared, thus before swelling (Table V.). Two such tests for the initial state were done in two different preparations to show the perfectly uniform concentration of gelatin in all parts of the gel before swelling.

The figures in Table V. show that even in 0·01 $N$ acid, a concentration gradient of the swollen protein structure is still apparent after six weeks and seems practically constant after the fourth week.

[13] See E. J. Cohn, *Physiol. Rev.*, **5**, 349, 1925 ; and *J. biological Chem.*, **63**, 721, 1925.
[14] Marinesco, *Equilibre de membrane. Actualités scientifiques.* *Ed.* Hezmann, Paris, 1934.

After the same length of time of immersion in very dilute alkali ($p_H$ 9 to 10) the concentration gradient is much more marked ; the average

TABLE V.—SOLUTION, $p_H$ 2·1 STRONG ACID — T°.   0 — 5° C. GM. GELATIN PER 100 GMS. OF GEL.

| | Cortex. | Nucleus. | $\dfrac{\text{Cortex}}{\text{Nucleus}} \times 100.$ | Average Concentration in the Whole Gel. |
|---|---|---|---|---|
| Initial state . . . . | 6·94 | 6·99 | — | 6·965 |
| Initial state (another preparation) . . . . | 6·49 | 6·48 | — | 6·485 |
| 1st week . . . . | 2·6 | 4·6 | 56 per cent. | 3·6 |
| 2nd ,, . . . . | 3·2 | 4·0 | 80 ,, | 3·6 |
| 3rd ,, . . . . | 3·2 | 3·8 | 84 ,, | 3·5 |
| 4th ,, . . . . | 3·1 | 3·6 | 86 ,, | 3·3 |
| 5th ,, . . . . | 3·0 | 3·5 | 86 ,, | 3·25 |
| 6th ,, . . . . | 3·0 | 3·5 | 86 ,, | 3·25 |

amount of gelatin in the cortex is 70 per cent. only of what it is in the nucleus, as previously mentioned. Therefore, the concentration at the centre itself is very definitely greater than at the surface.

## Conclusion.

1. Chemical reactions between gelatin and electrolytes in gelatin gels in equilibrium of diffusion with an aqueous solution give rise to a distribution which corresponds to Donnan's membrane equilibrium in the case of sodium chloride and of calcium chloride. The reactions are chiefly due to electrolytic dissociation of acid and basic organic radicals at the surface of the protein structure of the gel. In slightly acid solutions ($p_H$ 3 to 7), surface adsorption does not seem to come into account or hardly, in the case of the above mentioned ions. The situation is not generalisable to all electrolytes, namely not to magnesium sulphate.

2. In swollen blocks of gelatin gels, there is a concentration gradient of the micelles forming the protein structure of the gel and this determines, in turn, a concentration gradient of the diffusible ions in the gel at equilibrium of exchange with an aqueous solution. This uneven distribution of the gel constituents will maintain itself as long as the gel structure retains its elasticity.

*(Added when presenting the paper)* :

Concerning the study of the reaction between gelatin and magnesium sulphate, it should be mentioned that the determinations of the sulphate ion concentration in the gels were subject to a small error and that consequently the values for [$SO_4$] on Table III. are very slightly too high. The dry residue of the gels neutralised with $K_2CO_3$ having been directly ignited without the addition of an oxydising reagent, part of the organic sulphur content of the gelatin was removed during ignition. A small part of it, however, was held back in the ash. Several blanc determinations were made with isoelectric gelatin neutralised with $CO_3K_2$ in the absence of $MgSO_4$. The sulphur content in ash corresponded very consistently to about 100 mgs. of sulphur per 100 gms. of powdered isoelectric gelatin containing 14·7 gms. of $N$. per cent. Since the concentrations of the gelatin

in the gels at equilibrium of diffusion were known, it was possible to determine with sufficient approximation the corrected values.  The results are as follows (see Table III.) :

Expt. I.—The concentration of the sulphate ions equals about **62** instead of *63·6*.

Expt. II.—The concentration of the sulphate ions equals about **56·5** instead of *59·5*.

Expt. III.—The concentration of the sulphate ions equals about **27** instead of *29·7*.

TABLE VI.

| *t* Hours. | $\sqrt{t}$. | $p_{mm}$ | $K = p/\sqrt{t}$. | |
|---|---|---|---|---|
| 1 | 1 | 5 | 5 | |
| 2 | 1·41 | 6·5 | 4·6 | |
| 3 | 1·73 | 7·5 | 4·3 | |
| 6 | 2·45 | 10 | 4·1 | Conc. = Normal. |
| 7 | 2·65 | 10·5 | 4·0 | Average value of $K = 4·1$. |
| 8 | 2·83 | 11 | 3·9 | log $K = 0·613$. |
| 9 | 3·00 | 12 | 4·0 | |
| 25 | 5·00 | 18·5 | 3·7 | |
| 32 | 5·66 | 22·0 | 3·9 | |
| 49 | 7·00 | 26·0 | 3·7 | |
| 1 | 1 | 4 | 4 | |
| 2 | 1·41 | 6 | 4·2 | |
| 3 | 1·73 | 7 | 4·1 | |
| 6 | 2·45 | 9 | 3·7 | Conc. = $N/2$. |
| 7 | 2·65 | 9·5 | 3·6 | Average value of $K = 3·7$. |
| 8 | 2·83 | 10 | 3·6 | log $K = 0·568$. |
| 9 | 3·00 | 11 | 3·7 | |
| 25 | 5·00 | 17·5 | 3·5 | |
| 32 | 5·66 | 20 | 3·5 | |
| 49 | 7·00 | 24 | 3·4 | |
| 1 | 1 | 3 | 3 | |
| 3·7 | 1·92 | 6 | 3·1 | |
| 5·7 | 2·39 | 7 | 2·9 | |
| 7·7 | 2·78 | 8 | 2·9 | Conc. = $N/10$. |
| 22·7 | 4·76 | 12 | 2·5 | Average value of $K = 2·7$. |
| 27·7 | 5·26 | 13 | 2·5 | log $K = 0·431$. |
| 31·7 | 5·63 | 14 | 2·5 | |
| 46·7 | 6·83 | 17 | 2·5 | |
| 53·7 | 7·33 | 18·5 | 2·5 | |
| 93·7 | 9·68 | 24·5 | 2·5 | |
| 1 | 1 | 3 | 3 | |
| 3 | 1·73 | 3·5 | 2 | |
| 4 | 2 | 4 | 2 | Conc. = $N/100$. |
| 22 | 4·69 | 6 | 1·3 | Average value of $K = 1·6$. |
| 31 | 5·57 | 7 | 1·3 | log $K = 0·204$. |
| 46 | 6·78 | 7·5 | 1·1 | |
| 53 | 7·28 | 8 | 1·1 | |
| 93 | 9·64 | 10 | 1·0 | |

These very slight differences do not change anything to the conclusions drawn in the report.

The second part of my report deals with the rate of penetration of OH⁻ ions in gelatin gels from a very dilute NaOH solution.  After a certain time, the depth of penetration of the red colour in the cubes of gelatin gels stained with phenol red stays at a constant level somewhere about halfway

before reaching the centre of the cubes. I have considered this steady state as a true one rather than an extreme case of very slow rate of diffusion. As far as this interpretation is concerned, it is important to have an idea of the velocity of purely physical diffusion in such a case of very dilute NaOH solution in contact with a gelatin gel. From a comparison with the rate of diffusion of the same NaOH solution in acidified agar gels at the same temperature, I came to the conclusion that it did not concern an extreme case of very slow diffusion. But this comparison is not altogether satisfactory because both cases are not entirely comparable : in the case of the acidified agar gel, the acid diffuses out of the gel, whereas in the case of gelatin, the acid functions belong to the gel structure. There is another, probably a better method of estimating what the rate of purely physical diffusion of the very dilute base would be in the gel if no such equilibrium as the one I suggested tended to take place. This method consists in calculating the velocity of migration from data obtained in similar conditions at very much greater concentrations of the penetrating
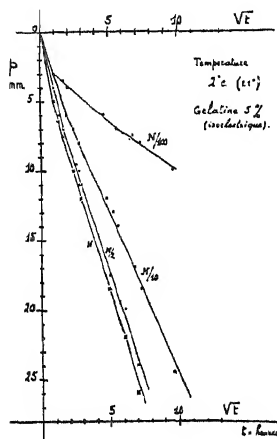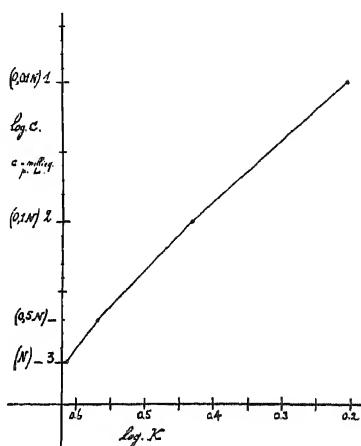


FIG. 3.                    FIG. 4.

base. When one is dealing with purely physical diffusion, the penetration is proportional to the square root of the time $(K = p/\sqrt{t})$ and if various values of $K$ are determined for different concentrations of the penetrating substance, the relation between log $K$ and log $C$ is a simple linear one. In other words, the ratio of two values of $K$ equals a certain power of the ratio of the corresponding concentrations :

$$\left(\frac{C_1}{C_2}\right)^n = \frac{K_1}{K_2}: \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

H. Sobotka and A. B. Sabin have verified these relations in the case of methylene blue, chromates and other coloured substances.[15] I have applied them to the case of NaOH solutions diffusing in columns of isoelectric gelatin gels at 2° C. Since the concentration of gelatin in the blocks of gel I used corresponds to 7 to 8 per cent. at the beginning of diffusion and falls to 2 to 3 per cent. after swelling, I adopted an average value of 5 per cent. gels in graduated cylinders. There was practically no swelling on account of adherence on the walls. The results are given on Table VI. and on Fig 3 for four experiments. The time is expressed in hours, the penetration $p$ in millimeters. The relation between the penetration and

[15] *J. Amer. Chem. Soc.*, **50**, 1561, 1928.

the square root of the time is not strictly linear. It is nearly so for concentrations of NaOH equal or stronger than $N/10$; for $N/100$ on the contrary, the curves show already a marked deviation from the linear relation: for $N$, $N/2$ and $N/10$ solutions, the maximum range of variation of $K$ is of the order of 20 to 30 per cent. of its average value; this is only a small variation in comparison with the 125 per cent. variation of the average value of $K$ when the concentration is $N/100$. Moreover, the relation between log C and log K is not strictly linear (Fig. 4). It is clear that the case of diffusion of a base in a gelatin gel is not a pure one of simple physical diffusion, unless one is dealing with very concentrated NaOH solutions. Let us, therefore, only take into account, in our calculation, the results plotted on the three first curves which are nearly linear [16] $(N, N/2, N/10)$; they will give us three values for $n$, namely 0·150, 0·183 and 0·196 with an average value of 0·18 $\left( n = \dfrac{\log K_1 - \log K_2}{\log C_1 - \log C_2} \right)$. This allows us to calculate from equation (1) what the value of $K$ would be for a NaOH solution $N/10,000$, provided purely physical diffusion of the same concentration level (change of colour of the indicator) would still take place throughout all parts of the gel at such low concentration. This value of $K$ (0·78) allows us, in turn, to calculate $t$ for any given value of $p$ in the same circumstances: $\sqrt{t} = p/0·78$ (for a solution of $p_H$ 10). The following results are obtained:

— for $p = $ 10 mm., $t =$ 7 days      (10 days).[17]
— ,, 12 ,, ,, 9 to 10 days) (2 weeks).[17]
— ,, 15 ,, ,, 17       ,, (3 weeks).[17]
— ,, 20 ,, ,, 28       ,, (5 weeks).[17]
— ,, 25 ,, ,, 1½ months (2 months).[17]

From these approximate determinations it appears that if purely physical diffusion of the concentration level corresponding to the change of colour from red to yellow took place in all parts of the blocks of gelatin gels immersed in dilute NaOH solution of $p_H$ 10, the following results would be obtained:
— a period of 1 to 2 weeks would be sufficient to obtain a penetration of the red colour of about 10 or 12 mm.
— a cube of gel 30 mm. wide (after swelling), would need less than 3 weeks to become uniformly red.
— a cube of 40 mm. would need a month to reach the same result, and one of 50 mm. about 1½ to maximum 2 months.
These indications are in contrast with the experimental results obtained. Some of these are as follows:

| | Size of the Cube of Gelatin Gel in mm. (after Swelling). | Duration of the Immersion in the Dilute NaOH Solution. | Penetration of the Red Colour in mm. from the Surface. |
|---|---|---|---|
| Cube No. I.   . | 40/50/50 | 7 weeks | 11 mm. |
| Cube No. II.  . | 40/40/55 | 2 months | 10 to 12 mm. |
| Cube No. III. . | 35/50/50 | 6 weeks | About 10 to 11 mm. |
| Cube No. IV.  . | 30/30/30 | 3 months | About 10 to 12 mm. |

After 1 month, or shorter time, it is not possible to give one single value. The penetration may vary from 5 to 9 mm. in different experiments. The

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[16] It is difficult to use stronger solutions than $N$, because they tend to dissolve the gel.

[17] The values between brackets give the time for $n = 0·20$ and $K = 0·65$ at $p_H$ 10. Since these calculations are based on curves which show already slight deviation from the linear relation, the values found for $t$ are certainly maximum values, probably too high.

state of the gel from one preparation to another is not always exactly the same, and during the 4 first weeks the swelling may be differently rapid and pronounced ; and this influences the rate of penetration at the beginning of diffusion. For this early period it is better to follow the penetration externally on the same block, although the readings are less accurate ; on Fig. 5 it is shown how the penetration progressed in one of the cases ; it is quite evident that there is no linear relation at all between the penetration and the square root of the time : the penetration becomes more rapid at the end of the first week on account of the fall of the protein concentration due to swelling, but after the second week the curve becomes rapidly horizontal as one approaches the steady state. In no instance has the penetration ever exceeded 10 to 12 mm., even after 3 months' diffusion. At the end of my report, I have given experimental evidence of a long-standing concentration gradient of the gelatin structure in blocks of gel immersed in 0·01 $N$ strong acid at 2° C. (Table V.). I may add now that after 12 weeks there is still 10 per cent. difference between the average concentration of gelatin in the cortex and in the nucleus of the blocks.

A concentration gradient of the protein structure of a gelatin gel thus takes place during the process of swelling. In the case here related it maintained itself at a permanent degree for several weeks and began to give way after more than 2 months' immersion, but was still apparent, however, after 3 months.



FIG. 5.—Rate of penetration of the red colour in a cube of an 8 per cent. gelatin gel stained with phenol red.

Abscissa. Time in days $(t)$.
Ordinates. Penetration in mm.
Solution. NaOH $= 0\cdot5 \times 10^{-3} N$ (constant).
Temperature. 2° C.

| | Before Immersion. | After 6 Days' Immersion. | After 49 Days' Immersion. |
|---|---|---|---|
| $a$ . . . | 25 mm. | 35 mm. | 45 mm. |
| Volume of block | 15·6 c.c. | 42·9 c.c. | 91·1 c.c. |
| Average concentration of gelatin. | 8 per cent. | 2·9 per cent. | 1·37 per cent. |

# DIFFUSION POTENTIALS AND MOBILITIES OF IONISED GELATIN. ACID AND NEUTRAL SOLUTIONS.

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Various estimates have been made of the mobilities of the gelatin ion on both sides of the isoelectric point. The principal methods available are (*a*) conductivity, (*b*) migration, using the Hittorf method, (*c*) cataphoresis, (*d*) diffusion potentials. Methods (*a*) and (*b*) have been freely applied to various proteins, *e.g.*, by Pauli and his co-workers and the results should agree provided that the distribution of the various kinds of ampholyte ions which have been postulated is not materially altered under the different experimental conditions. This applies particularly to method (*c*). Method (*d*) has only occasionally been applied, and then with different aims. The application to acid and neutral solutions is the subject of the present paper.

Hydrogen potentials, $E_H$, of chains such as :

$H_2Pt \mid H_2SO_4$ 0·1 $N$., $x$ per cent. gel
$\mid H_2SO_4$ 0·01 $N$., $x$ per cent. gel $\mid H_2SO_4$ 0·01 $N$. $H_2Pt$
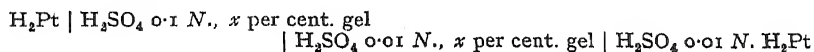
or sulphate potentials, $E_{SO_4}$, of the same solutions having electrodes Hg, $Hg_2SO_4$, were measured by Ferguson and France, 1921.[1] The diffusion potential was calculated from those of the chains by the equation :

$$E_d = \frac{2E_{SO_4} - E_H}{3}.$$

The transport number of the anion was shown to increase from 0·187, characteristic of the pure acids, to 0·685 as the concentration '$x$' of gelatin was increased and the hydrogen ion was progressively replaced by the gelatin ion. Diffusion potentials, calculated as above, sank from + 0·0254 when $x = 1$ to − 0·046 when $x = 20$. For reasons which it is not necessary to particularise here, none of these results were suitable for calculating the mobility of gelatin. More useful data from the present point of view were obtained by Ferguson and Bacon, 1927.[2] The chains measured were of the type :

HgHgClKCl sat. $\mid$ HCl 0·1 $N$. $\mid$ HCl 0·1 $N$, gel $x$ per cent.

$\xrightarrow{E_1}$
$\mid$ HCl 0·01 $N$, gel $x$ per cent. $\mid$ HCl 0·01 $N$. $\mid$ KCl sat. HgClHg
$\xrightarrow{E_2}$ $\xleftarrow{E_3}$
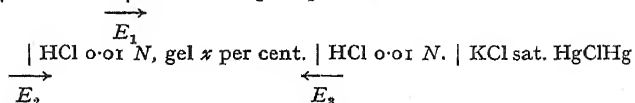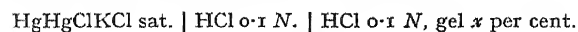
Additional saturated potassium chloride, calomel electrodes could be inserted at various points, and the diffusion potentials could therefore be measured separately. Liquid junctions were formed in a stop-cock and were of a static character. It was shown that the potentials obtained

[1] Ferguson and France, *J. Amer. Chem. Soc.*, **43**, 2150.
[2] Ferguson and Bacon, *J. Amer. Chem. Soc.*, **49**, 1921, 1927.

on adding varying quantities of gelatin bore a general resemblance to those of corresponding sodium chloride, hydrochloric acid, mixtures. The potentials $E_1$, starting from zero where $x = 0$, rose with additions of gelatin to a maximum and nearly constant value of 40 mv. when $x = 10\cdot9$. Potentials at $E_3$ in the opposite direction changed from 0 to $31\cdot5$ as $x$ increased from 0 to $1\cdot09$ per cent., then remained nearly constant on further additions. From both these results, it appears that gelatin chloride consists of 1090 g of the dry protein combined with 1 equivalent of acid.

Consider first the junction $E_3$, when $x = 1\cdot09$. A solution made from $1\cdot09$ g of gelatin and 10 c.c. of $0\cdot10$ N. HCl in 100 ($9\cdot17$ c.c. of $0\cdot10$ N. HCl to 1 g of gelatin) appears from the combination curves of several investigators to have $p_H = 2\cdot9$, $[H^\bullet] = 1\cdot26 \times 10^{-3}$. Since the total concentration is $1\cdot09 \times 10^{-2}$, $[Cl'] = 9\cdot64 \times 10^{-3}$ and $[\text{gel}^\bullet] = 7\cdot4 \times 10^{-3}$. In the $0\cdot01$ N. HCl, $p_H = 2\cdot02$, $[H^\bullet] = [Cl'] = 9\cdot64 \times 10^{-3}$. Applying the Henderson equation (1) below and using $Fu_{H\bullet} = 347$, $Fv_{Cl'} = 75\cdot5$ (both at $25°$), also assuming that the mobility of the gelatin ion is zero.

$$E = 59\cdot1 \log \frac{u_1c_1 + v_1c_1}{u_2c_2 + v_2c_2} = 32\cdot2 \text{ mv.}$$

Since this is greater than the observed potential, a finite value, e.g., $Fu = 10$, may be assigned to the gelatin ion.

Then $E = 0\cdot0591 \times 0\cdot5180 = 30\cdot5$ mv. Since the experimental value is $31\cdot5$ mv. it appears that the mobility lies between 0 and 10.

Potentials $E_2$ between the $0\cdot10$ N. and $0\cdot01$ N. solutions both containing gelatin increased from $+ 40$ mv. characteristic of the pure acids, to a maximum of $+ 55$ at $1\cdot09$ per cent. of gelatin, when the $H^\bullet$ of the more dilute acid is practically completely combined, they then diminished rapidly, changed sign and became about $- 40$ mv. at $x = 10\cdot9$ per cent. of gelatin, and when $x = 12\cdot24$, $E = - 39\cdot8$ mv. If these solutions contained gelatin chloride in the ratio 10 : 1, then the application of the simple formula would give :

$$E = 39\cdot8 = 0\cdot0591 \frac{v - u}{v + u} \log \frac{c_1}{c_2}$$

and the mobility $u$ ($Fu$) of the gelatin ion would be $16\cdot7$. But it may be shown that the hydrogen ion should have had a considerable effect in this case also. Although $[H^\bullet]$ of the $0\cdot01$ N. solution was probably reduced nearly to the isoelectric value by the large excess of gelatin, yet the more concentrated solution must have had a considerable hydrogen ion concentration, since the equivalent of $8\cdot3$ c.c. of $0\cdot1$ N. HCl had been added to each 1 g of gelatin. From the neutralisation curve, $p_H$ may be estimated as $2\cdot4$, $[H^\bullet] = 4 \times 10^{-3}$. Assuming a 90 per cent. dissociation of the $0\cdot1$ N. gelatin chloride and 100 per cent. in the $0\cdot01$ N. solution, ionic concentrations may be calculated in the usual way and introduced into equation (1) p. 351. If $Fu$ ($\text{gel}^\bullet$) $= 15$, $E_{II\rightarrow I} = - 24\cdot5$ mv. If $Fu = 0$, then $E = - 37\cdot3$ mv. It appears from this that the mobility of gelatin is very low in these high concentrations.

Some of the uncertainties of these results could be avoided by working along rather different lines. If the concentrations of all ions are kept below $0\cdot01$ N., degrees of dissociation and activity coefficients calculated by any method are nearly equal and not far from unity. It was also arranged that the diffusion potentials should be due as far as possible to differences between mobilities of the ions of gelatin and those of the opposite ions having the same sign.

## Acid Gelatin Solutions.

Solutions of gelatin chloride and of potassium chloride were made and adjusted so as to fulfil as closely as possible the following conditions :

(1) $p_H$ about 3 ; (2) isohydric and isoionic in chlorine ; (3) therefore having nearly the same concentrations of gelatin and of potassium ion.

In these two solutions, represented as I. gelatin and II. potassium, the concentrations and activities of the ions were calculated and determined experimentally by various methods.   I. was a 1 per cent. gelatin solution to which was added 6·5 c.c. per 100 of 0·1 $N$. HCl, so that it was 0·0065 $N$. in total chlorine.   $p_H$ derived from some of the combinations mentioned below, was 3·14.   II. was made from 5·5 × 10⁻³ $N$. KCl which was made 1 × 10⁻³ $N$. with respect to HCl.   The $p_H$ was 3·04.   The conductivities determined at 25·0° by the Kohlrausch method were : I. 7·1 × 10⁻⁴, II. 11·1 × 10⁻⁴, reciprocal ohms.   The conductivity of II. calculated from limiting ionic mobilities is 11·8 × 10⁻⁴.   Hence the degree of dissociation $\alpha_0$ is 0·945, a value which may also be attributed to the gelatin solution. Activity coefficients $\gamma$ may be calculated by the simplified equation :

$$\log \gamma = 0.5 \sqrt{\mu},$$

in which $\mu$ is the ionic strength, whence $\gamma = 0.99$.   From the tabulated values of Lewis and Randell,

$$\gamma_{H\cdot} = 0.976, \ \gamma_{K\cdot} = \gamma_{Cl'} = 0.918.$$

The following chains were measured :

(1) $H_2$Pt | HCl gel || KCl sat. || KCl sat. | HgCl Hg
(2) $H_2$Pt | HCl gel || KCl sat. || KCl sat. | $H_2$Pt
(3) $H_2$Pt | HCl KCl || KCl $N$. || HgCl Hg
(4) Ag AgCl | HCl KCl || KCl sat. || KCl 0·1 $N$. | AgCl Ag
(5) Ag AgCl | HCl KCl || KCl $N$. || HCl gel | AgCl Ag.

With regard to (3) and (5) it may be remarked that KCl 1·0 $N$. was frequently substituted for KCl sat. in salt bridges, and the KCl 1·0 $N$. calomel for the KCl saturated calomel electrode.   This solution was sufficiently concentrated to eliminate diffusion potentials of such dilute solutions, and was less likely to alter their concentrations by diffusion.   Single potentials of the 1·0 $N$. KCl calomel electrodes are taken as 0·283 volts at 25·0°.

Combinations (4) and (5) give the concentrations of the chlorine ion. Taking $p_{Cl'}$ in 0·1 $N$. KCl as 1·135₆, chain (4) gave $p_{Cl'} = 2.206$ in II., and chain (5) gave $p_{Cl'} = 2.376$ in I.

These and the preceding activities were introduced into the following equations.

The Henderson equation may be expressed as :

$$E_{II \to I} = \frac{RT}{F} \frac{(U_1 - V_1) - (U_2 - V_2)}{(U'_1 + V'_1) - (U'_2 + V'_2)} \ln \frac{U'_1 + V'_1}{U'_2 + V'_2} \quad . \quad (1)$$

in which    $U_1 = \Sigma u_1 c_1$ in I.    $U_2 = \Sigma u_2 c_2$ in II.
$V_1 = \Sigma v_1 c_1$ in II.    $V_2 = \Sigma v_2 c_2$ in II.

and $V'$, etc., refer also to multivalent ions $= \Sigma nuc$. Gelatin ion is treated as univalent thus deducing an apparent mobility $Fu$ for each charged centre on the molecule.

If it is assumed to a first approximation that $\Sigma v_1 c_1 = \Sigma v_2 c_2$, $i.e.$, $[Cl']_1 = [Cl']_2$, then the equation refers to two solutions having a common ion (Planck) and is simplified to :

$$E_{II \to I} = \frac{RT}{F} \ln \frac{(\Sigma u_1 + v)c_1}{(\Sigma u_2 + v)c_2} \quad . \quad . \quad . \quad (2)$$

$$= \frac{RT}{F} \frac{\lambda_1}{\lambda_2} \text{ or } \frac{x_1}{x_2} . \quad . \quad . \quad . \quad (3)$$

Arbitrary values for $Fu_{gel^+} = 0, 10, 15, 20$ may be assigned in making these calculations. Zero mobility of the gelatin ion will give a maximum value to $E$. Mobilities of other ions at $25\cdot0°$ are : $H^• = 347$, $K^• = 74\cdot7$, $Cl' = 75\cdot5$.

(1) From the uncorrected concentrations $[H^•]_1 = [H^•]_2 = 1 \times 10^{-3}$ $[Cl']_1 = [Cl']_2 = 6\cdot5 \times 10^{-3}$, $[K^•]_2 = 5\cdot5 \times 10^{-3}$, combined with the above mobilities, the value of $E$ calculated from equation (2) is $-10\cdot2$ mv., or the gelatin side should be positive by this amount if gelatin has zero mobility.

(2) From the conductivities, using equation (3), $E = -11\cdot8$ mv.

(3) The potentiometric results give the following ion activities

$$a_{H^•_1} = 7\cdot24 \times 10^{-4}, \quad a_{Cl'_1} = 4\cdot2 \times 10^{-3},$$
$$a_{H^•_2} = 9\cdot12 \times 10^{-4}, \quad a_{Cl'_2} = 6\cdot2 \times 10^{-3}.$$

If $a_K$. in II. is taken as being equal to the difference between those of the chlorine and hydrogen ions it is $5\cdot3 \times 10^{-3}$. Several other assumptions could have been made without materially affecting the results.

On introducing these values into equation (1) we obtain :

$$Fu \ gel^+ = \quad 0 \qquad 10 \qquad 15 \qquad 20$$
$$E_{II \to I} = \quad -9\cdot5 \quad -8\cdot23 \quad -7\cdot64 \quad -6\cdot9$$

## Measurement of Diffusion Potentials.

The chains measured were usually of the type :

HgHgClKCl $1\cdot0$ $N$. | KCl $1\cdot0$ $N$. agar | HClKCl | HCl gel
| KCl $1\cdot0$ $N$. agar | KCl $1\cdot0$ $N$. | HgCl Hg
$E$

Normal KCl electrodes were preferred to saturated for the reasons already stated, potentials were verified by the occasional use of saturated KCl electrodes. At $E$ the diffusion potentials were produced. These were either of the static or flowing junction type. The gelatin side was always positive as required by theory.

Static junctions were formed in a connecting tube which contained initially only HCl KCl solution. When introduced into the above chain, the potentials (means of several readings) were $11\cdot0$ and $10\cdot5$ millivolts. Occasionally higher readings were obtained. Hydrogen electrodes introduced into solutions I. and II. gave potentials (a) with diffusion 15 mv.; (b) without diffusion 5 mv. The difference 10 mv., is the diffusion potential.

Flowing junctions were made in an apparatus already described [3] which was constructed according to the principles stated by Lamb and Larson, McInnes and Yeh, and Scatchard. The means of several experiments gave $E = 13\cdot5$, $13\cdot8$, $13\cdot9$ mv.; after standing one hour, $13\cdot0$.

It will be observed that all measured potentials are higher than those calculated even on the assumption that the gelatin ion has zero mobility. A satisfactory explanation of this is difficult to find. Inactivation of the chlorine ion in solutions of true proteins has been postulated by several workers, cf., Gram and Cullen [4] but the calculated diminution in the product $v_1c_1$ of the chlorine ion in solution I. merely has the effect of slightly reducing the calculated potential. Also Pauli and Safrin [5] can find no evidence of inactivation of *univalent* anions by glutose.*

[3] Prideaux, *Far. Soc. Trans.*, **24**, 11, 1928; **25**, 1, 1929.
[4] Gram and Cullen, *J. Biol. Chem.*, **57**, 487, 1923.
[5] Pauli and Safrin, *Biochem. Z.*, **233**, 86, 1931.
* Glutose is gelatin purified by washing followed by electrodialysis and autoclaving at $125°$ for periods up to 1 hour.

On the assumption that mixture does not occur but that the static junction is one in which the ions are present in their natural diffusion gradients, potentials should be calculated by the Planck formula. Differences between the results obtained by the two formulæ, however, are relatively slight. It has been already shown that the results of Ferguson and Bacon [1] lead to an unexpectedly low value (between 0 and 10) for the mobility at a $p_H$ of about 3, in which part of the combination curve cataphoretic results show a maximum velocity of at least 2·7 $\mu$/sec., volts/cm. Prideaux and Howitt, [6] which corresponds to an effective mobility of 2·7 $\times$ 9·5 = 25·5 per unit positive charge on the gelatin ion. See also König and Pauli [7] who obtained mobilities of the same order by the Hittorf method in the case of other proteins. Cataphoretic velocities, however, are measured at a high potential gradient which imposes a steady motion on the gelatin molecule ($m = 10,000$) and it is doubtful whether Stoke's law is applicable to the low potential gradients which prevail in the diffusing layer. In this the gelatin molecule may behave as if it had a very low mobility, the diffusion potentials being determined solely by the other ions. The potential calculated from the conductivities by equation 3 is also too high, in spite of the fact that the most probable error, due to the calcium ions in the gelatin ash, would give too high a conductivity to solution I., and therefore too low a potential.

### Mobilities from Conductivities.

Calculation of gelatin mobilities from electrical conductivities by the standard methods yield higher results. Thus Pauli and Safrin [5] assign a mobility between 10 and 20 in a solution 2·77 $\times$ $10^{-3}$ $N$. with respect to HCl. Assigning a value $p_H = 4.4$ from the known combination curve, and a degree of dissociation $\alpha_c = 0.95$ for all salts, the mobility $Fu$ comes to 17·4. Similar calculations in acetate solutions also show a high mobility.

### Acetate Solutions.

A buffer solution II. was made 0·02 $N$. in total acetic acid and 0·0012 $N$. in sodium acetate, which had a measured $p_H = 3.60$. Measured and calculated ion concentrations were :

$[H^{\bullet}] = 2.5 \times 10^{-4}$, $[Na^{\bullet}] = 12.1 \times 10^{-4}$, $CH_3CO'_2 = 14.8 \times 10^{-4}$.

Solution I. contained 0·8 per cent. of gelatin with 0·02 per cent. of acetic acid, and hydrochloric acid was added until $p_H$ was 3·62. Ion concentrations were :    $[H^{\bullet}] = 2.4 \times 10^{-4}$    $[Cl'] = 25.82 \times 10^{-4}$,    $CH_3CO'_2 = 15.50 \times 10^{-4}$, and by difference $[gel^{\bullet}] = 38.92 \times 10^{-4}$. Conductivity calculated at 25·0° for ions other than gelatin is 3·42 $\times$ $10^{-4}$ while that found was 4·77 $\times$ $10^{-4}$ leaving 1·35 $\times$ $10^{-4}$ for that of the gelatin ion, which therefore had the high mobility of 34·8.

The diffusion potential $E_{II. \rightarrow I.}$ as calculated by equation (1) if $Fu_{gel^{\bullet}} = 0$ is $-$ 20 mv. the high value being due to the partial replacement of $CH_3CO'_2$ by $Cl'$ in solution I., which increases the potential due to unequal mobilities of gelatin and sodium ion. If, however, a mean mobility of 30 is assigned to the former ion, the diffusion potential becomes $-$ 11·9 mv. Measured values were $-$ 9·0 with static and $-$ 9·5 with the flowing junction. Conditions at the junctions are evidently very different in the acetate and the chloride solutions. In the acetate series, solution II. is buffered.

[6] Prideaux and Howitt, *Proc. Roy. Soc.*, **126A**, 126, 1929.
[7] König and Pauli, *Biochem. Z.*, **252**, 325, 1932.

## Neutral Solutions.

Effects due to inequalities in [H$^{\cdot}$] would be eliminated by keeping all solutions at or near the neutral point, at which gelatin exists as the gelatinate ion " gel " with a relatively high electrical surface density. Its mobility could then be measured against that of the chlorine ion having as nearly as possible the same concentration.

Gelatin, freed from ash as usual by the method of Loeb, after treatment with the volume of standard KOH required to give a neutral solution was diluted with conductivity water so as to give a 1 per cent. solution, which was 0·0028 $N$. with respect to K$^{\cdot}$. Hydrogen potentials were measured against a normal KCl calomel electrode having a calculated single potential of 0·2825 volts at 17°. Hence the single potential of the hydrogen electrode was found to be 0·428 volts $p_{\mathrm{H}} = 7\cdot48$. In solution I., [H$^{\cdot}$] $= 3\cdot3 \times 10^{-8}$, K$^{\cdot} = 0\cdot0028$, gel $= 0\cdot0028$. In solution II., [K$^{\cdot}$] $=$ [Cl$'$] $= 0\cdot0028$.

Diffusion potentials at a static junction were measured as already described. The gelatin side was negative as required by theory. $E_{\mathrm{II.} \rightarrow \mathrm{I.}}$ was $+ 15\cdot0$ mv.

Calculations from equation I. or II. above gave the following results :

If $\qquad V = 0 \qquad 10 \qquad 15 \qquad 20 \qquad 30$
$\qquad\qquad E = 18\cdot0 \quad 14\cdot75 \quad 13\cdot2 \quad 11\cdot8 \quad 9\cdot25$

In a static junction, therefore, the mobility of gel appears to be about 10.

*Added (when presenting the paper)*: The flowing junctions of two other gelatin solutions having measured $p_{\mathrm{H}}$ values of 6·2 and 6·45, gave potentials of 6·3 and 6·45 respectively, in an apparatus with large tap of the type described by Ferguson, Van Lente, and Hitchens, 1932.[8] The potentials sometimes began at about 2 mv. (owing perhaps to mixing), and after closing the tap and restarting the flow on the next day rose to the steady values given above, which according to the preceding calculation, correspond to a mobility of the gelatin anion between 30 and 40.

In conclusion, the author wishes to express his obligation to Dr. F. O. Howitt and Dr. D. E. Woods for valued co-operation in parts of this work, and to the Research Committee of University College, Nottingham, for a grant towards the purchase of apparatus.

## GENERAL DISCUSSION.*

**Dr. E. Heymann** (*London*) said : Professor Elöd suggests the formation of hydroxides when metal salts with tanning properties react with gelatin, the hydroxide probably being the tanning substance, instancing the case of cobalt salts. I would like to mention some investigations on reactions of several metal salts with gelatin in diluted solution,[1] which may give some further support to Professor Elöd's conclusions.

If a gelatin solution is mixed, for instance, with an iron chloride solution and a small amount of the intermicellar liquid is produced by ultrafiltration, this ultrafiltrate contains less iron than chlorine ; whereas in the case of reactions between gelatin and the (neutral) salts of the alkaline or alcaline earth metals, the ultrafiltrate contains the anion and the cation in equivalent amount.

I also investigated the heat of those reactions. It is positive, but very

[8] Ferguson, Van Lente and Hitchens, *J. Amer. Chem. Soc.*, **54**, 1279, 1932.
* On five previous papers.
[1] E. Heymann and F. Oppenheimer, *Biochem. Z.*, **199**, 468, 1928 ; E. Heymann, *Kolloid-Z.*, **50**, 97, 1930.

small (about 100-500 cal. per gm. equiv. of bound metal salt) in the case of the reactions of gelatin with alkaline and alkaline earth salts. But the heat of the reactions between gelatin and the hydrolysing salts of iron, aluminium and zinc is much greater and has a negative sign (order of magnitude : — 2000 cal.). It is very likely that this negative heat is due to the hydrolytic decomposition of those salts, which occurs simultaneously with the reaction with the protein, the hydrolysis being the only endothermic process which is likely to occur. In the case of iron chloride solutions the well-known slow hydrolysis, which does not reach an equilibrium for many months, takes place in a few minutes when proteins are present.

Furthermore, if we investigate the reaction of iron chloride, not with the colloidal compound gelatin, but with a simple amino-acid, we also find an endothermic reaction yielding as a final product an iron hydroxide sol, which regarding the chemical composition of the particles and some colloidal properties is very similar to ordinary iron hydroxide sols.

All these results can be easily understood if we assume that those metal salts which are capable of hydrolytic decomposition are at least partially transformed into hydroxides when reacting with gelatin.

**Professor Evert Gorter** (*Leiden*) said : As the two first points raised by Miss Jordan Lloyd are applicable to the experiments on the spreading of proteins, I should like to show you very briefly some of our results.[2]

A protein spreads only in a layer of minimal thickness (6·7·5 Å.) at the isoelectric point and at a high acid (or alkaline) reaction. On both sides of the isoelectric point minima are observed. This means that an ionised protein has less tendency to spread than a *zwitterion* or a protein-salt.

It is possible to obtain spreading at the $p_H$ which show minima in the curve, in which $p_H$ is plotted against size of spreading area, by adding to the water in the tray different ions. These phenomena are most easily studied with *pepsin and trypsin*.[3] Trypsin has an iso-electric point at $p_H$ 7·0, and therefore it is easy to study the influence of the addition of negative ions on the acid side of this point, *e.g.* at a $p_H$ 4·0.

A maximal spreading is obtained by adding univalent ions, *e.g.* Cl, in amount to make the solution 40 millimolar whereas bivalent ions produce the same effect in a 1 millimolar solution, and trivalent ions give the same result in a 1/40 millimolar concentration. For pepsin having its iso-electric point at $p_H$ 2·7, the minimum lies at $p_H$ 4·0, and here the addition of positive ions produces the same effect. The valency rule holds good also here.

Instead of using ordinary bivalent ions such as $SO_4$ or Ca, we can make use also of organic substances, *e.g.* glutathione, or tartrazin as acids or spermidin as bivalent base.

We can prepare compounds of proteins and this latter class of substances.[4] Take a tartrazin-ovalbumin compound, obtained by adding tartrazin to an ovalbumin solution. If to an ovalbumin-solution of 5 mg./c.c., we add tartrazin to make the solution 5·6 millimolar, the product no longer shows a minimum on the acid side of the iso-electric point ($p_H$ 4·6).

[2] E. Gorter and F. Grendel, *Trans. Faraday Soc.*, **22**, 477, 1926.
[3] Kindly given to me by Dr. John Northrop. For details see E. Gorter *J. gen. Physiol.*, January, 1935.
[4] Unpublished.

Adding smaller quantities gives a compound which shows curves in between that of ordinary ovalbumin and the above-mentioned complex.

It seems possible to explain by these experiments the type of curve one gets with some proteins. I will give as an example the curve of insulin,[5] which has the same form as that of a tartrazin-ovalbumin
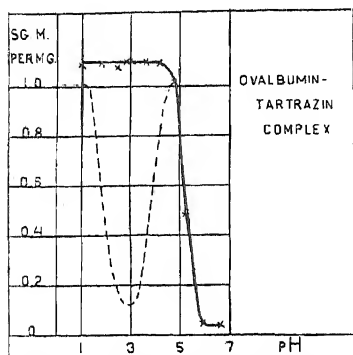


FIG. 1.—Tartrazin-ovalbumin.
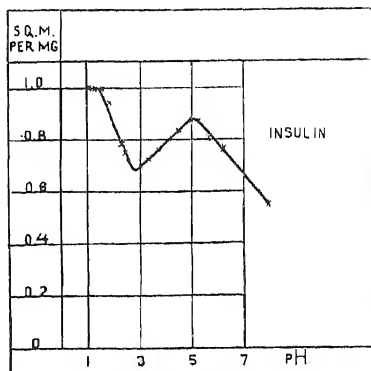


FIG. 2.—Insulin.

compound, in which some $NH_2$ are left unoccupied by the tartrazin. This suggests that in insulin a strong acid is fixed to the $NH_2$ groups.

That the explanation of the spreading of proteins given here is correct, can be shown by the result obtained with a *tripeptide of α-amino caprylic acid* [6] which Dr. Th. M. Meyer has succeeded in synthesising in my laboratory. Whereas "natural" peptides like the tetrapeptide of alanin, or the tetra- or pentapeptide of leucine do not spread, this tripeptide spreads perfectly well, owing to the greater length of the chains (8 C atoms). On this tripeptide we were able to show also a distinct influence of $p_H$ on the spreading on both sides of a rather distinct maximum, and also here it is easy to show that the addition of bi- or trivalent positive or negative ions, will produce a maximal spreading when added to the water in the tray in small amounts (1/5 millimol per litre for methanetrisulfonic acid at $p_H$ 2·7, and 8 millimol per litre for magnesium chloride at $p_H$ 8·0).
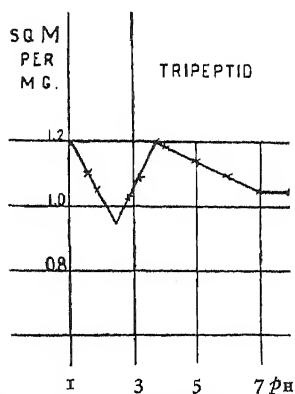


FIG. 3.—Tripeptid.

As all these observations very well illustrate the first two points of the introduction of Miss Jordan Lloyd, it seemed interesting to discuss them here.

**Dr. K. Söllner** said : The experiments of Professor Gorter seem to me most interesting, yet there is one point, which appears to me a little bit doubtful : Are the films in all cases quite homogeneous ? For

[5] E. Gorter and J. van Ormondt, *Kon. Akad. v. Wetenschappen, Proceedings*, **36**, 922, 1933.

[6] E. Gorter, Th. M. Meyer, G. Th. Philippi, *Kon. Akad. v. Wetenschappen, Proceedings*, **37**, 355, 1934.

Zocher and Stiebel [7] have shown by ultramicroscopic investigations, that sometimes the films of some proteins are not homogeneous, but contain a greater or smaller amount of colloidal particles, depending upon the $p_H$ of the water on which the film is spread and—of course—upon the nature of the proteins themselves.

**Professor Gorter,** in reply, said: Inhomogenity of the films is only found at or near the minima. They can also be detected by measuring potential differences with a movable electrode above these films.

**Mr. E. Hatschek** (*London*), with regard to Professor Bigwood's paper, wished to raise a point which might appear trivial to those unfamiliar with diffusion experiments, *viz.* the use of a cube. Diffusion into spaces with discontinuous boundaries gave results which could not be interpreted, as the diffusion front did not remain similar to the boundary but gradually approached a spherical form; in addition the cube itself changed its shape, the faces becoming curved. The only suitable bodies were spheres, the casting of which offered no great difficulties, or cylinders with the end faces rendered impermeable (*e.g.* clamped between greased glass plates). For diffusion through the cylindrical surface the speaker had shown experimentally that the advance of the diffusion front followed the simple square root law.

**Dr. G. S. Adair** (*Cambridge*) said: The observations on clupein made by Dr. Linderstrøm-Lang show that this substance may be of importance for the experimental study of colloidal electrolytes, since it may fill the gap between the simpler ions of low valence and the more complex systems usually investigated, where the size or the charge of the particles are functions of many variables. The calculation of the ionic strength is made by the term $c_p n_p$, where $c_p$ is the concentration and $n_p$ is the valence of the colloidal ion, and not by the term $c_p n_p^2$. There is no doubt that the term $c_p n_p$ is consistent with the measurement of titration curves, in the range of concentrations referred to, but in my opinion, it is probable that in the case of exceedingly dilute solutions where the distances between the ions are large in comparison with their size, the contribution of the colloidal ions to the ionic strength may be greater than $c_p n_p$.

**Professor E. J. Bigwood** (*Brussels*) said: The possibility of the formation of co-ordination complexes at the amino groups of proteins such as suggested by Miss Jordan Lloyd is exceedingly interesting. It seems that my results of the study of the reactions between magnesium sulphate and gelatin in the gel state show an example of such a type of reaction. They show namely that between $p_H$ 3 and 7, gelatin in the gel state reacts with $Na^+$, $Ca^{++}$, or $Cl^-$ ions like ordinary electrolytes (electronic valence). With $MgSO_4$ the results were still the same at $p_H$ below 4·8. But at the iso-electric point and at $p_H$ above 4·8, the results were different. More Mg and more S were found in the gel than was expected. As possible explanation, I suggested the possibility of the formation of some type of complex compound, or surface adsorption. Miss Jordan Lloyd's suggestion of the possibility of formation of co-ordination complexes at the amino groups of a protein may probably explain my results with $MgSO_4$. First of all, the fact that $MgSO_4$ only behaved abnormally at and above a $p_H$ value corresponding to the iso-electric point is very suggestive in this respect, because one would

expect that the possibility for the formation of the above-mentioned complex would only exist at and above $p_H$ 4·8, that is to say, when the amino group is free and does not behave as a base $(RNH_2)$ ; whereas in acid solutions of $p_H$ below 4·8 the complex cannot be formed because the amino group acts as a base $(RNH_3OH)$. When the complex is formed, the situation may be pictured as follows :—

|  | gel | solution |
|---|---|---|
| 1. At $p_H$ 4·8 (iso-electric point) : | $SO_4Mg . H_2N\ P$ <br> $MgSO_4$ | $MgSO_4$ |
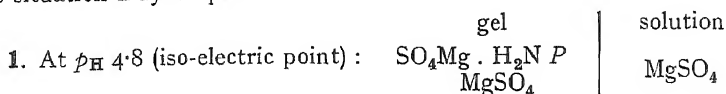
Instead of finding equal amounts of $MgSO_4$ in both phases, one must find more $Mg^{++}$ and more $SO_4 =$ in the gel than in the solution. This is what was found (expt. II, Table III.).

|  | gel | | solution |
|---|---|---|---|
|  | II | I |  |
| 2. At $p_H$ between 4·8 and 7 : | $SO_4Mg . H_2N\ P$ COOMg <br> $MgSO_4$ <br> $H_2SO_4$ | | $MgSO_4$ <br> $H_2SO_4$ |
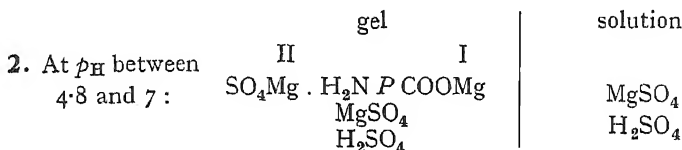
If reaction I took place alone (no complex formation), one should find more Mg and *less* S in the gel than in the solution. If, however, reaction II does take place (complex formation) and if it is predominant, one should find more Mg *and more* S in the gel than in the solution, since the ash determinations give the total amount of these elements in the gel. This is also what was actually found (expt. III, Table III). The assumption that such a type of complex is formed between gelatin and $MgSO_4$ at $p_H$ 4·8 and above, gives us a better explanation of my results than surface adsorption, because if we were dealing with this last eventuality, there would be no reason to believe that surface adsorption of $MgSO_4$ would not take place at $p_H$ below 4·8 as well as it would above or near 4·8.

In reply to Dr. Hatschek : The diffusion coefficients were determined in columns of gelatin gels, except in one case, in which the measurement was made for comparison in a cube. Since this comparison was made to obtain an order of magnitude and not a very precise value, it may be considered as certain that differences of shape of the surface of the gels has no importance in my experiments. From my observations in columns of gels it was calculated that at very much lower concentration of the penetrating ion, the penetration in the cube should have been after several weeks very much greater than it was found to be. Such differences as a few days or a few weeks can certainly not be explained by differences in shape of the surface of the gel.

**Dr. Jordan Lloyd** (*London*), in reply, stated : It is very interesting that Professor Bigwood, working on diffusion experiments, should find evidence that magnesium sulphate behaves differently from sodium or calcium chlorides. Magnesium chloride was one of the salts for which Leuthardt suggested the formation of a co-ordination complex with amino-acids. The suggestion that the magnesium sulphate may be forming co-ordination complexes with the gelatin at the iso-electric point seems, therefore, very plausible. Professor Gorter's very interesting work on protein films brings evidence in support of the theory of protein-salt complex formation from a very different field of work. His experiments with insulin showing that it behaves in the spreading of a film more like a protein-tartrazin complex than like a pure protein

is surely one of the most striking discoveries in the colloidal chemistry of this very interesting and important substance.

As regards the criticisms made by Herr Neuberger on the value of the two ends of a titration curve made over a long range of $p_H$, these, of course, are perfectly valid.  As the $p_H$ of the system becomes very high or very low, experimental errors increase and theoretical deductions take on a more dubious quality.  The new method of Dr. Schofield, that is, titrating with meta-phosphoric acid can, therefore, be regarded as one of the most important advances in the technique of protein titration made recently, since his system is one which automatically simplifies itself as he adds more acid instead of becoming more complicated as usually happens.  Herr Neuberger's technique of titrating in the presence of alcohol has the same advantages.

Nevertheless protein titrations by the old-fashioned method of using hydrochloric acid and sodium hydroxide have yielded results in the hands of different workers that lie remarkably close together. Professor Elöd asks whether titration curves are always the same for different kinds of gelatin—no, they certainly are not identical but they are very similar and the limits in which the recorded results lie do not approach the curve given for collagen.  This curve, curiously enough, both in the values of its ordinates and in its general form, is remarkably like a curve for another fibrous protein, namely wool keratin, recently published by Speakman.

# COLLOIDAL ELECTROLYTES IN PHOTOGRAPHY.*

By Fritz Weigert (*Leipzig*).

## 1.

The rôle of colloidal electrolytes in photography can only be rightly estimated when their properties are investigated under the same conditions as those existing during the photographic operations : exposure and developing.  These conditions obtain only in a dried or swollen silver halide-gelatine emulsion coating.  In such a solid or semi-solid system the mobility of the individual particles is practically completely suspended and the ordinary methods of investigation fail, *e.g.*, observation of coagulation, peptisation and of electrophoretic effects.  Other means must accordingly be sought to give information as to the structures and properties of the colloidal electrolytes of importance to photography.

These substances are constructed in a very complicated manner out of the various components of the photographic emulsion—binding material, silver halide, silver, silver sulphide, dyestuffs and various electrolytes—being " micelles," in the sense of the definition of Cotton, Mouton, Ducleaux and Zsigmondy, which are capable of being transformed in an intramicellar manner by the exposure and the subsequent treatment without any material change in size or position occurring. For their investigation which will simultaneously help to elucidate the

* For references and further experimental and theoretical details on the same subject, see F. Weigert, *Photogr. Korresp*, **70**, 1934, Beilage VI., p. 41.

mechanism of the photographic processes, the study of the light sensitivity and optical properties of the systems seems suitable.

## 2.

In every photographic emulsion more or less large crystal grains of silver halide can be observed microscopically and, after exposure and development, black grains of silver are found in their place.    Together they represent the *granular phase* of the emulsion.    The free spaces between these grains are not resolvable, even under the highest microscopic and ultramicroscopic magnifications, and this amicroscopic region comprises the *intergranular phase.*

The light sensitivity of the silver halide crystals has in recent years been the subject of important and thorough investigations by the chemists and physicists of all countries, and can be regarded as a matter settled as to its essentials.    The results of the experiments, especially of those on crystals the structure of which is well understood, show that the primary action of the light leads to the separation of an electron from the halogen ion and to its acceptance by a neighbouring silver ion.    The photochemical primary process is therefore the photolysis of silver halide with formation of a silver and a halogen atom :

$$(1) \quad Br^- + h\nu = Br + \theta.$$
$$(2) \quad \theta + Ag^+ = Ag.$$
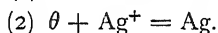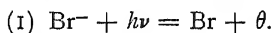
The effective energy quanta correspond to the absorption region of the halide crystals.    Colloidal electrolytes play no part in this primary process, which takes place within the granular phase of the emulsion.

We are now in a position to show that the *intergranular phase* of a photographic emulsion is also light sensitive, and that this property is dependent on the colloidal micelles mentioned above.    As a series of photographic effects is very closely simulated by the light sensitivity of the micelles, we are of the opinion that it is here that the real primary process of  photography takes place, only affecting the grains of the granular phase secondarily.    This conception we have summarised as the " micelle theory of the developable latent image," and it will here be described briefly because it, at the same time, provides information as to the structure of the colloidal electrolytes important in photography.

## 3.

The method chiefly used for the investigation of the micelles consists of the measurement of their dichroitic properties, concerning which it is known from Wiener's theory of mixtures that they can only occur in a system the individual particles of which are smaller, as regards their dimensions and distances apart, than light waves.    As this property involves the impossibility of microscopic and ultramicroscopic resolution, it follows that this impossibility having been taken as the criterion of the intergranular phase, the observation of any dichroitic phenomenon provides a proof that the phenomenon is taking place in this phase, which may also be termed the micellar phase.

Two dichroitic effects suitable for the exploration of this phase exist —*film dichroism* and *photodichroism*.    The film-dichroism of the photosensitive layer has been interesting us for some time.    It appears during the oblique observation of the dry layers, and is caused by the fact that the

anisotropic and dichroitic micelles, stained by metallic silver, are pre-ferentially orientated with their axes in the plane of the film but with no orientation of their azimuths. Layer dichroism is accordingly to be interpreted statistically by the large number of particles conforming to Wiener's '$s$ criterion. Its sign will be taken so as to refer to the optical axes of the anisotropic micelles. The film dichroism will therefore be *positive* when, with oblique or almost tangential transmission of the light, the extinction is greatest for that ray which vibrates preferentially in the *plane of the film*. To measure film dichroism the film to be examined is observed, according to a method to be described elsewhere, in a polarisa-tion apparatus with a monochromator, the light passing through at 45°.

*Photodichroism* results when the coloured elementary particles on which film dichroism depends are also light sensitive. Those particles of which the strongest absorption direction coincides with the direction of vibration of the polarised radiation then in general change in colour in polarised light most quickly, and the trace of this colour change, *selective with respect to its azimuth*, remains in the exposed film in the form of photodichroism. Its sign is *positive* when the absorption has *increased* for the direction of vibration of the exciting radiation, *negative* when the absorption has decreased.

We have observed that all dry photographic coatings exhibit a more or less strong film dichroism after development. Clear transparent emulsions, in addition, exhibit after excitation with polarised light a photo-dichroism, which also occurs very generally with silver chloride, bromide and iodide when any chemical or physical developer is used. We are therefore in a position to investigate the intergranular, or micellar, phase photographically.

<div align="center">

**4.**

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The actual explanation of the structure of the amicroscopic micelles was, it is true, provided, not by the photographic experiments, but by simpler photochemical ones on collodion and gelatin films stained with dyestuffs. Matulis has during recent years examined very many such systems with respect to their dichroism. The results, considered in the light of extensive previous experiments, led to the following general scheme for the structure of light sensitive micelles :—

The seats of the anisotropy are the anisotropic unit particles of the binding medium, gelatin or collodion, and the seats of the dichroism the molecules of adsorbed substances to which the colouring is due. Therefore it is always a question of micelles constructed of several dif-ferent components. They are light sensitive when absorption of a light quantum excites a chemical reaction among the components of the micelle, these components usually interacting with one another so that the structure and the optical properties of the micelle are changed by the illumination.

As the film dichroism and the photodichroism of photographic coatings is in thorough qualitative agreement with the effects observed with dyestuff systems, the general scheme of the structure of the dyestuff micelles may be applied to the photographic micelles as well.

<div align="center">

**5.**

</div>

For the elucidation of their special structure, we utilise a further experiment, first carried out by the Japanese workers Horiba and Kondo.

A gelatin plate, for the preparation of which the gelatin has been to a high degree freed from chloride ions by thorough washing with conductivity water and which contains 0·001 equivalents of silver nitrates per 100 cm.² of surface, is illuminated with white light. The plate remains practically as colourless as before. But on adding the slightest traces of chloride ion, of the order of $10^{-8}$ equivalents, a rapid browning by reduced metallic silver occurs. Horiba and Kondo state that this great photochemical acceleration is one of the most sensitive reactions for chloride ions. Bromide and iodide ions are less effective. The quantitative analytical study by Matulis of these processes demonstrated the surprising fact that far more silver atoms can be produced than there are chloride ions present in the film. The small amount of silver chloride therefore acts as a catalyst for the photochemical reduction of the excess of silver ions by the reducing groups of the gelatine. As in addition, the finely divided metallic silver produced acts as an optical autosensitiser, a highly complicated mechanism must certainly underlie what is apparently so simple a process.

The investigation of the photodichroism simultaneously appearing during irradiation with polarised light showed, qualitatively, in the first place, that light sensitive *micelles* are involved in the photochemical reaction. The sign of the photodichroism, however, varied according as light of short or long wave-length was used for excitation. In the first case it was weakly positive, indicating therefore that the anisotropic molecules orientated parallel to the direction of vibration of the exciting radiation are more strongly coloured by silver, which agrees with the analytically determined increase of the amount of silver. In red light the film was, at first, not light sensitive, but it became so when some silver had been formed by short-wave blue radiation, the silver then acting as a sensitiser for red light. The photodichroism was then strongly negative. This shows that a decrease took place in the silver content of the micelles, anisotropic and stained by silver, which were orientated parallel to the direction of vibration of the radiation. It could, however, be proved analytically that in purely red light the total amount of the silver present in the film remained unchanged. The silver which, before the red irradiation, was situated on the anisotropic gelatin particles must therefore be present in other parts of the system after irradiation.

### 6.

Let us summarise the results described in the previous section for silver nitrate gelatin :—

(1) Traces of silver chloride are necessary for the photochemical reduction of silver ions.

(2) Far more silver atoms are produced than there are chloride ions present.

(3) The silver acts as an autosensitiser.

(4) Irradiation with blue polarised light produces weakly positive photodichroism. This involves an increase in the amount of silver.

(5) Irradiation with red polarised light produces strongly negative photodichroism. For this the film must already contain some silver, the amount of which is, however, not affected by the red irradiation.

If, in addition, it be taken into consideration that the whole process takes place in a dry film in which the micelles are not capable of movement and that only the gelatin can act as reducing agent, then the following scheme can be developed for the reaction mechanism :—

The light sensitive unit micelle forms a unit structure in the gelatin micelle, and on it is adsorbed a monomolecular layer of silver chloride, after which come a number of layers of silver ions, which are present in large excess (state I). The photochemical process then proceeds in the following stages :—

I. $\overset{+}{Ag}$ | $\overset{-}{Cl}$ | $\overset{+}{Ag}$ | $\overset{+}{Ag}$ | $\overset{+}{Ag}$

II. $\overset{+}{Ag}$ | $\overset{-}{Cl}$ | ● | $\overset{+}{Ag}$ | $\overset{+}{Ag}$

III. $\overset{+}{Ag}$ | $\overset{-}{Cl}$ | $\overset{+}{Ag}$ | ● | $\overset{+}{Ag}$

IV. $\overset{+}{Ag}$ | $\overset{-}{Cl}$ | ● | ● | $\overset{+}{Ag}$

V. $\overset{+}{Ag}$ | $\overset{-}{Cl}$ | $\overset{+}{Ag}$ | ● | ●

VI. $\overset{+}{Ag}$ | $\overset{-}{Cl}$ | ● | ● | ●
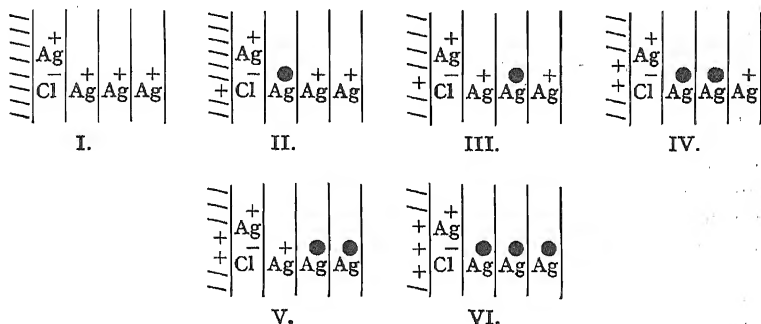
(a) In the short-wave light an electron first passes from the chloride ion to the adsorbed silver ion, as assumed by Fajans for his silver system (*Silberkörper*). A silver atom [1] and a chlorine atom is thus produced, the latter immediately oxidising a reducing group of the gelatin and thus being converted again into chloride ion. The micelle has thereby passed over into the state II, in which the oxidation of the gelatin is symbolised by the positive charge ($+$).

(b) In this state, II, red light, too, can be effective, owing to the formation of the silver atom, capable of absorbing in the long-wave region. A red quantum can now separate an electron from the silver atom and the electron will be trapped by a neighbouring silver ion. The micelle passes into the state III, which only differs from II by the increased distance of the silver atom from the gelatin. The light absorption of the micelle is hereby decreased in the red (negative photodichroism) but the amount of silver remains constant.

(c) A *Silberkörper* system has now, in the state III, been reformed, so that an electron can, in the light, again pass from a chloride ion to the neighbouring silver ion, and thus allow a second silver atom to be produced. An autosensitisation, therefore, takes place by stages. The elementary micelle is now in the state IV.

(d) By means of two electron transfers from a silver atom to a neighbouring silver ion, the two silver atoms can, under the continued action of light, move towards the right (state V) and thus allow

(e) The same chloride ion to give up its electron for the third time, so that a new silver atom might be formed. This causes the micelle to pass into the state VI. These stages can, under the influence of light, repeat themselves for as long as silver ions and reducing groups for the regeneration of the chloride ions are still available within the micelle.
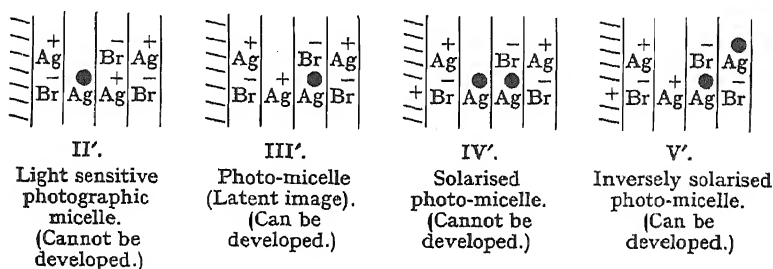
## 7.

The gelatin with silver nitrate is a photographic printing out system, which already to begin with, contains the, admittedly bad, developer,

[1] In the diagram of the scheme the silver *atoms* are distinguished by Ag.

the gelatin.    Actual photographic emulsions are developed after exposure by an added reducing agent.    First the latent image is formed by the illumination.    But the mechanism of the action of the light is the same as with the silver nitrate gelatin.

The framework of the unit micelle of a silver bromide emulsion corresponds to model I, in which the free silver ions are replaced by silver bromide molecules, which are either still free or have already fallen into their place in the crystal lattice.    In the latter case, the micelle is continuous with a silver bromide crystal.    Such a micelle is, however, not yet photographically sensitive to visible light.    For this there must be formed during the ripening of the emulsion some metallic silver by chemical reduction or some silver sulphide by the interaction of silver bromide with sulphur-containing constituents of the gelatin.    Both of these can act as sensitisers, without which modern photography would be inconceivable.

| II'. | III'. | IV'. | V'. |
|---|---|---|---|
| Light sensitive photographic micelle. (Cannot be developed.) | Photo-micelle (Latent image). (Can be developed.) | Solarised photo-micelle. (Cannot be developed.) | Inversely solarised photo-micelle. (Can be developed.) |

The photographic, light sensitive micelle under discussion, therefore, has the structure II' corresponding to model II, in which the silver atom can be replaced by a silver sulphide molecule.    By the absorption of a light quantum in the absorption region of the adsorbed silver atom an electron transfer is brought about, leading to an interchange of places between an atom and a neighbouring silver ion, so that the state III' is produced.    This we will describe as a " photo-micelle," regarding it as the real *substance of the latent photographic image.*    A very plausible mechanism for the development of the silver bromide in this positively charged state has recently been published by Schwarz.    He drew attention to the experimental fact that all really useful photographic developers contain a reducing *anion.*    This holds not only for the organic developers, but also for the inorganic ferrous oxalate.    The reducing anions are adsorbed by the silver bromide, which, in the photo-micelles, is charged positively, and can reduce them to metallic silver.    When irradiated further the photo-micelles (III') pass over into the state IV', whereby the silver ion is discharged, again a silver atom being produced.    This renders the photo-micelle undevelopable, and we then have a *solarised micelle.*    Still further illumination can produce the state V', in which the photo-micelle, as it again contains a positive charge, is also developable again.    This is the well-known photographic phenomenon of the double reversal of the solarisation.

When silver sulphide molecules are present as sentitisers they lose one electron in the light, and allow silver ions to be produced.    When sensitising dyestuff molecules have also been adsorbed, they give up the energy of excitation taken up in their absorption region to a neighbouring silver atom or silver sulphide molecule and sensitise the electron emission

by a second order collision. In both cases the same photo-micelle III′ is produced.

## 8.

A quantitative interpretation of most photographic effects is furnished by further observation resulting also in the study of photodichroism from experiments by Stiebel. He was able to show that the photo-micelles are not by themselves sufficient for development, and that for this there are necessary also heterogeneous silver nuclei, which can be produced secondarily by the collecting together of the silver atoms present in neighbouring photo-micelles.

The whole of the blackening curve may now be explained by the *joint effect of the rates of formation* of the photo-micelles and of the silver nuclei, which promote development as *initiators ;* these two obey different laws. For the production of photo-micelles from the light sensitive micelles, Einstein's photo-chemical equivalent law holds. But the formation of the silver nuclei is determined by the probability that the photo-micelles are produced sufficiently close together, so that the silver atoms can easily collect together. But in addition silver can be produced in short-wave light by the direct photolysis of silver halide discussed in paragraph 2. In this joint effect of the photo-micelles and the silver nuclei on the developing is to be found the reason for the existence of a threshold value, for the various forms of the blackening curves, for the increase of the light sensitivity in the short-wave spectrum region (because photolysis of the silver bromide predominates there) and for a series of other photographic effects which are discussed in detail in the paper quoted above.

All these discussions find their experimental justification in phenomena the seat of which is, in view of the occurrence of dichroitic effects, in the amicroscopic micelles. The capacity for being developed is then transferred to the microscopic silver bromide crystal grains when a photo-micelle also happens to form part of the surface of a crystal, according to III′, *i.e.*, when photo-micelle and crystal are in molecular contact. We therefore consider that, by taking into account light sensitive colloidal electrolytes, which is what is represented by our micelles, the various photographic phenomena have to a considerable extent been interpreted.

The means by which this end has been attained have at the same time shown that it is possible, by the use of optical and photo-chemical methods, to elucidate the structure also of immobile micelles in solid systems.

## GENERAL DISCUSSION.

**Professor A. J. Rabinovitch** (*Moscow*) said that the extremely interesting physical phenomenon discovered by Professor F. Weigert— the photodichroism of photographic emulsions—may not be closely related to the mechanism of latent image formation and development. Especially on this last point the speaker (A. J. R.) has his own views expressed in his recent papers in the *Zeitschr. f. wissensch. Photogr.* Professor Weigert has not adduced any experimental evidence which could convince the speaker that his own theory of development is wrong. Therefore he cannot fully adhere to the views exposed by Professor Weigert.

At the same time, the remarkable photodichroitic Weigert-effect, which has not found yet its full explanation, presents a very great interest from the physical point of view, and ought to be studied systematically, may be also in absence of binding medium.

**Dr. H. Neurath** (*Wien*) said : I want to add a few words about some results we got in an impromptu, unpublished investigation on gelatin. We tried to find out the relationship between the colloid-chemical qualities and the photographical application of photographic gelatin. Comparison of measurements of conductivity, $p_H$, viscosity, swelling and amount of ash led to the conclusion that photographic fogs are due to the presence of gelatoses and amino acids. A gentle electrodialysis, removing these products, diminishes these fogs, in addition to decreased sensitivity. I should be very interested to know, if Professor Weigert could bring in accordance these results with his experience.

**Dr. S. O. Rawling.** (*London*) *communicated*: Some years ago I discovered that the sensitivity of a washed photographic emulsion could be depressed by the addition of acid. The change in sensitivity appeared to be extremely rapid and was largely reversible.[1] Various considerations have led me to believe that the chemical changes which give rise to this effect occur in the environment of the crystals of silver halide and not in the crystals themselves. Professor Weigert believes the seat of sensitivity to be in the environment of the crystals, and I should therefore be interested to know whether his theory provides a simple explanation of the effect which I have described.

**Professor F. Weigert** (*Leipzig*) replied : The very interesting *reversible* effect of $p_H$ on the light-sensitivity of photographic emulsions discovered by Dr. Rawling seems to be a good example for the application of the Micellar-Theory to practice.

The transfer of an electron from a silver atom to a silver ion after absorption of a light quantum, which changes a light sensitive micelle (II′) into a Photomicelle (III′) is accompanied by an expulsion of a silver ion from the silver halide. This egression of a positive charged ion is rendered more difficult if there are hydrogen ions in the neighbourhood (low $p_H$), and the light sensitivity will be lowered. It is facilitated by large $p_H$. This effect of environment must be largely reversible.

At the same time there exists a slow *irreversible* effect, also observed by Dr. Rawling, which acts in the same sense. For a low $p_H$ renders difficult the formation of silver atoms by the reducing groups of gelatin during ripening, and a large $p_H$ facilitates it. The gelatoses and aminoacids, studied by Dr. Neurath, are probably good reducing agents to produce silver and therefore favour light-sensitivity and fog in photographic emulsions.

[1] The experiments were described in the following papers : Rawling and Glasset, *Phot. J.*, **66**, 495, 1926; Rawling, *ibid.*, **67**, 42, 1927; Rawling, *ibid.*, **69**, 83, 1929.

# INTERACTIONS OF PROTEINS AND NUCLEIC ACID.

BY T. CASPERSSON, E. HAMMARSTEN AND H. HAMMARSTEN.

The purpose of this paper is to investigate some possible means of showing an eventual protein structure in cell nuclei, especially in chromosomes. It must be regarded as a preparatory experiment with an exclusively practical aim.

The reactivity of nucleic acid (in this paper always nucleic acid from thymus) to protein must, from a theoretical viewpoint, be considered to be very strong. This is corroborated by the behaviour of these substances. It was shown long ago [1] that nucleic acid forms almost insoluble compounds with proteins on the acid side of their isoelectrical points and that these compounds are salts between nucleic acid and proteins. The reactivity of nucleic acid to lanthanum ions is also strong; the latter form compounds from $p_H$ 1 to 7, which are almost insoluble,[2] whereas the salts with dyestuffs have a considerable solubility. It is also very well known, that sulphosalicylic acid forms almost insoluble salts with proteins on the acid side of their iso-electrical points; on the other hand lanthanum ions and proteins do not react on the "acid side." The basic proteins histons and protamins form almost insoluble compounds (salts) with nucleic acid in equilibrium with a fluid of neutral reaction.[3] The interactions of dyestuffs, proteins and nucleic acid have been examined by numerous investigators.[4] In a homogeneous solution, containing a basic salt of nucleic acid and albumin, both lanthanum ions and sulphosalicylic acid will cause precipitations of compounds between proteins and nucleic acid.[2] The red blood corpuscles from *Triton* which, in the ultramicroscope, are almost optically empty (Fig. 1), will therefore be precipitated both in the nucleus and in the protoplasm (Fig. 2) by sulphosalicylic acid, whereas only the nucleus will be precipitated by lanthanum salts (Fig. 3). The outlines of the cells in Figs. 2 and 3 could be seen in the microscope but did not show up very well in the photographs. They have partly been drawn in with dotted lines. In all instances, where a precipitation took place, it was observed that the nuclei were precipitated *before* the precipitation in the protoplasm began. Other experiments showed that cell nuclei at a certain ill-defined stage can be entirely free from proteins Fig. 4). These red blood corpuscles from *Triton* had been treated with

[1] E. Hammarsten, *Z. physiol. Chem.*, **109**, 141, 1920 ; *Bioch. Z.*, **144**, 1924 ; *Acta Med. Scandinavica*, **68**, 1928.

[2] E. Hammarsten and T. Teorell, *Acta Med. Scandinavica*, **68**, 226, 1928.

[3] E. Hammarsten, *Bioch. Z.*, **144**, 5/6, 1924 ; Steudel, *Z. physiol. Chem.*, **72**, 305 ; **73**, 471 ; **83**, 72 ; **87**, 207, 1913 ; **90**, 298, **109**, 141, 1920. E. and H. Hammarsten, *Arkiv Kemi., Mineralogi och Geologi*, **8**, Nr. 27 ; H. Hammarsten, *Bioch. Z.*, **147**, parts 5/6, 1924.

[4] E. Hammarsten, G. Hammarsten and T. Teorell, *Acta Med. Scandinavica*, **68**, 219, 1928, etc.

sulphosalicylic acid in the same way as those in Fig. 2. The only differ-
ence was that the animals had been starved for three months and then
fattened for eight to ten days according to the prescriptions of Jolly [5]
to obtain cell divisions in the circulating blood. Cell divisions appeared
(Fig. 2, $X$), and at about the same time up to 90 per cent. of the red blood
corpuscles could not be precipitated in the nuclei by sulphosalicylic
acid as is usual (Fig. 2, normal). This phenomenon was very transient,[6]
and would disappear rapidly in an animal from which blood was with-
drawn at intervals. These results stimulated to further research.

It seemed advisable first to make *trial experiments* with proteins and
nucleic acid. In the first series (1) of these experiments solutions of proteins
and the sodium salt of nucleic acid were precipitated with (*a*) lanthanum
salt + malonic acid in high concentration; (*b*) zinc acetate + formalin
+ sodium chloride. In the second series (2) we attempted to digest, with
proteolytic enzymes, mixtures of proteins and the sodium salt of nucleic
acid. This mixture was obtained either by precipitating a solution of
the components with alcohol or with Carnoy. In order to prevent the
formation of a soluble salt of nucleic acid the digestive fluids contained
lanthanum acetate in various concentrations. The purpose of these experi-
ments was the following :—

1. (*a*) The strong activity of the nucleic acid may be blocked by a
very high concentration of an acid with a weaker activity. Malonic
acid has a comparative high dissociation constant ($1\cdot6 \times 10^{-3}$), and
can be dissolved in water up to 6 $N$. The $p_H$ of the fluid in equilibrium
with the precipitates in the experiments, where this reagent was used for
precipitating the lanthanum nucleinate from a solution of sodium nucleinate
and proteins, was always about $0\cdot9$. At this $p_H$ the amount of lanthanum
nucleinate in solution is nil, when measured by the quantity of phosphorus
in the fluid according to Pregl or by a colorimetric method.[7] It was
thought that when nucleic acid was precipitated in this way, the proteins
would remain in solution. (*b*) After treatment with formalin the proteins
are chiefly acids and ought to be precipitated by zinc ions, especially when
their solubility is diminished by saturation with sodium chloride. The
nucleic acid should be left in the solution as its zinc salt is soluble.

2. When a solid mixture of proteins and the sodium salt of nucleic
acid or a salt of these in a solid state is digested with proteolytic enzymes
(according to Waldschmidt-Leitz) at about neutral reaction, the proteins
ought to go into solution as digestion products, which do not form in-
soluble salts with nucleic acid. Of course the nucleic acid then must form
soluble salts; that can be prevented by lanthanum ions, whose con-
centration must be adjusted to be high enough to form the insoluble salt
of nucleic acid without too largely depressing the digestive power of the
enzymes. It is also necessary in experiments with cells to destroy the
" endo-enzymes " which, we think, will be effected by Carnoy- or alcohol
fixation, combined with heating. Some proteins, *e.g.*, albumin and globulin
must be denatured before they are treated with proteolytic enzymes, be-
cause they are resistant to digestion in the natural state. The solution
containing the proteolytic enzymes must be absolutely free from poly-
nucleotidases. Fortunately they are so, when prepared, according to
the method of Waldschmidt-Leitz, from pancreas and mucous membrane
from duodenum.

By making use of the enzyme-lanthanum reagent (**At-La**) or the lan-
thanum-malonic-acid-reagent (**Ma-La**), it ought to be possible to detect
protein structures in the cells by photographing at such a wave-length

[5] J. Jolly, *Arch. Anat. Micro.*, **6**, 455, 1904.
[6] E. Hammarsten and T. Teorell, *Acta Med. Scandinavica*, **68**, 237, 1928.
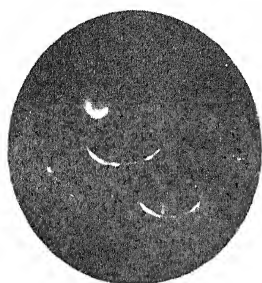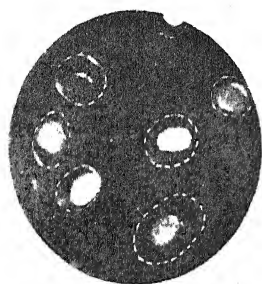[7] T. Teorell, *Bioch. Z.*, **230**, 1, 1931.

$X$
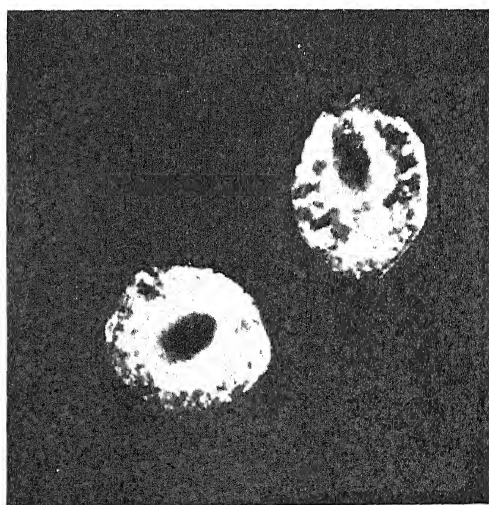↓

FIG. 1.

normal ↗

FIG. 2.

FIG. 3.

FIG. 4.

[*See page* 367.

FIG. 5.
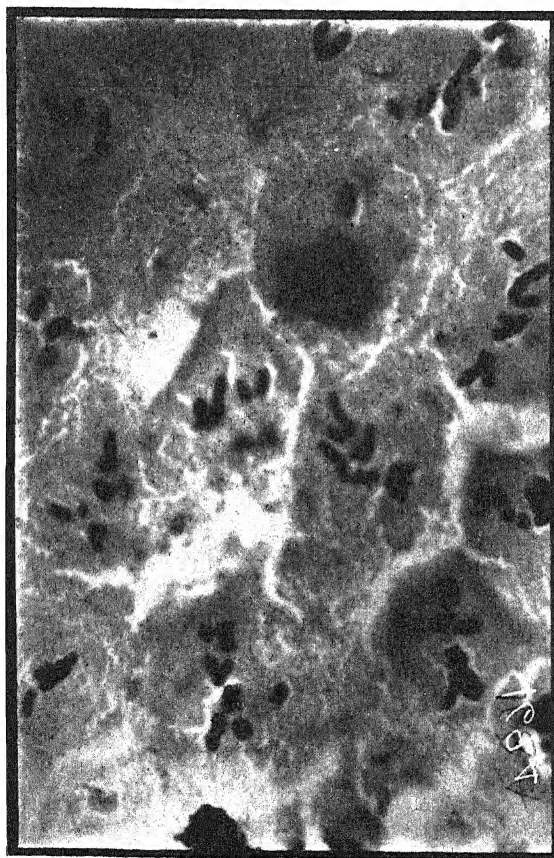


FIG. 6.



FIG. 7.

that the proteins absorb a sufficient amount of light. The structure would then appear as a decrease in the degree of blackening. Many difficulties will undoubtedly arise by the application of an analysis of this sort. Some of these will be discussed later by T. Caspersson. The quartz microscope necessary for that analysis, is as yet imperfect in regard to the lighting apparatus. As yet we have only been able to work with magnesium light at very short wave-length. This line is double, and therefore the pictures are not clear. The proteins absorb very little light, whereas the nucleic acid has a maximum of absorption at this wave-length. Although the experiments on cells are as yet very incomplete, and we have not been able to photograph in the proper light at all, we give some examples in Figs. 5 to 7 before we refer to our real experiments, the model experiments with proteins and nucleic acid.

Figures 5 to 7 represent microphotographs of sections (Carnoy-fixation, paraffin) from testicular cells (*Stenobotrus-species*), photographed : Fig. 5 in visible light ; Fig. 6 in magnesium light (in all other respects identical with Fig. 5) ; Fig. 7 in magnesium light after digestion with enzyme-lanthanum-reagent (magnification 4500). After digestion the chromosomes do not seem to show any new variation in the degree of blackening, which might be considered an indication of a protein-structure. However, if this supposed structure had the form of a close (eventually molecular) packing, it could only be seen or measured as an evenly distributed diminishing of the degree of blackening. With wave-length used the additional absorption from the proteins is insignificant and no difference at all can be expected in the degree of blackening in these chromosomes before and after digestion, where the nucleic acid has a maximum of absorption. If the proteins had been packed as solid proteins at intervals in the chromosomes, such a structure would have shown up directly in this light and also in visible light after digestion with our reagents. It seems that Professor T. H. Morgan has found chromosomes with such a structure. At his Nobel lecture in Stockholm, June 1934, he showed very long chromosomes, which had been treated with strong acetic acid, and these chromosomes had a transverse, ribbon-like structure. Although Morgan did not say so, we think that this ribbon-like structure indicated the negative of a protein structure in these chromosomes, seeing that his concentrated acetic acid is the equivalent of our malonic acid-lanthanum-reagent. If one assumes that the genes consist of the known substances, there are only the proteins to be considered, because these are the only known substances which are specific for the individual. *On that assumption a protein structure in chromosomes takes on a very great interest.*

### Trial Experiments with Proteins and Nucleic Acid.

1. (a) *Malonic acid + lanthanum -acetate and formalin + zinc-acetate.*

Lanthanum-malonic acid reagent (**Ma-La**) : HCl $N/1$   .   .   3·0 c.c.

| | |
|---|---|
| Malon. acid 6 $N$ . | 4·0 ,, |
| Lant. acetate 0·2 $N$ . | 2·5 ,, |
| Aq. dest. . . | 10·5 ,, |
| | 20·0 ,, |

This amount of the reagent was poured, while stirring, on to about 2 gr. of exactly weighed solutions of protein (four times crystallised serum-albumin, electrodialysed and entirely freed from phosphorus and $SO_4$, and concentrated in collodium tubes by gas-pressure), and sodium nucleinate, each being carefully weighed in the form of solutions. The precipitate in each test was very carefully treated with a glass-rod to get it in equilibrium with the solution, filtered and then washed with 2 × 5 c.c. of the reagent. This was not allowed to act upon the nucleic acid for more than twenty minutes. The precipitates were analysed (Table I.).

Phosphorus was determined in each test according to the methods of Pregl and of Teorell.[7] In all the following determinations only Pregl's method was used, when not otherwise mentioned. The determinations given throughout this paper were made with the utmost care, and the figures given are always averages from several well-agreeing determinations. The nucleic acid nitrogen was calculated from the phosphorus-value from

## TABLE I.

| | Number of Experiment. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1. | | 2. | | 3. | | 4. | |
| | *a.* | *b.* | *a.* | *b.* | *a.* | *b.* | *a.* | *b.* |
| **Before precipitation:** | | | | | | | | |
| Total protein nitrogen, mgm. | 1·06 | 1·06 | 2·67 | 2·71 | 5·13 | 5·46 | 9·45 | 9·36 |
| Total nucleic acid nitrogen, mgm. | 1·94 | 1·95 | 1·73 | 1·76 | 1·11 | 1·21 | 0·71 | 0·70 |
| **In the precipitate :** | | | | | | | | |
| Protein nitrogen, mgm. | 0·51 | 0·50 | 0·54 | 0·63 | 0·00 | − 0·06 | −0·06 | 0·00 |
| Protein nitrogen (as percentage of the total nitrogen) in the precipitate | 19·62 | 19·38 | 21·16 | 24·42 | 0·00 | 0·00 | 0·00 | 0·00 |

## TABLE II.

| | | | | |
|---|---|---|---|---|
| Weight of preparation, mgm. | 35·3 | 39·8 | 29·4 | 28·5 |
| Phosphorus, mgm. | 0·353 | 0·398 | 0·294 | 0·285 |
| Nitrogen, mgm. | 4·78 | 5·39 | 3·98 | 3·86 |
| Protein nitrogen, mgm. | 4·18 | 4·71 | 3·48 | 3·38 |
| Time of treatment in hours | ½ | 1·0 | 2·0 | 4·0 |
| **Undissolved :** | | | | |
| Nitrogen, mgm. | 0·75 | 0·84 | 0·64 | 0·61 |
| Phosphorus, mgm. | 0·339 | 0·355 | 0·280 | 0·273 |
| Quotient N/P . | 2·21 | 2·35 | 2·28 | 2·23 |
| Nitrogen, removed, mgm. . | 4·03 | 4·55 | 3·34 | 3·25 |
| Phosphorus removed, mgm. | 0·014 | 0·043 | 0·014 | 0·012 |
| Removed protein (as percentage of total protein) | *96* | *95* | *95* | *96* |

the factor $N/P = 1·69$, and the protein nitrogen was calculated as the difference between total nitrogen and nucleic acid nitrogen in the precipitates. In all cases the nucleic acid was quantitatively precipitated.

These experiments show that it is possible to block the basic groups in protein by an acid in a very high concentration, forming a soluble salt with nucleic acid. That was only possible, under the conditions of the

experiments, up to a degree. When the concentrations of the nucleic acid become too high, part of the protein, about 20 per cent. of the nitrogen in the precipitate, which is about the same as 20 per cent. of the total weight and probably of the volume too—will be precipitated with the lanthanum-malonic acid-protein-compound.

In order to ascertain how far it would be possible to remove protein from a precipitate containing protein and nucleic acid (the latter, being present as a salt with sodium or with protein), for later experiments on cells, it was thought best to use fixation with Carnoy.   37 gr. of a 3 per cent. solution of the sodium salt of nucleic acid (T) + 88 gr. of a 15 per

TABLE III.—P = 3·81 PER CENT.; N = 15·98 PER CENT.; PROTEIN NITROGEN = 9·54 PER CENT.; N/P = 4·20.

| | Number of Experiment. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1. | | | 2. | | | 3. | | |
| | a. | b. | c. | a. | b. | c. | a. | b. | . |
| Weight of preparation, mgm. | 30·0 | 31·6 | 38·3 | 36·4 | 33·4 | 30·3 | 34·3 | 33·0 | 30·7 |
| Phosphorus, mgm. | 1·146 | 1·202 | 1·456 | 1·390 | 1·267 | 1·160 | 1·308 | 1·266 | 1·169 |
| Nitrogen, mgm. | 4·79 | 5·05 | 6·12 | 5·82 | 5·34 | 4·84 | 5·48 | 5·27 | 4·91 |
| Protein nitrogen, mgm. | 2·86 | 3·01 | 3·65 | 3·47 | 3·19 | 2·89 | 3·27 | 3·15 | 2·93 |
| Time in hours of treatment . | ½ | ½ | ½ | 4 | 4 | 4 | 19 | 19 | 19 |
| **Undissolved :** | | | | | | | | | |
| Nitrogen, mgm. | 2·30 | 2·23 | 2·62 | 2·41 | 2·14 | 1·93 | 1·86 | 1·74 | 1·64 |
| Phosphorus, mgm. | 1·143 | 1·204 | 1·459 | 1·390 | 1·273 | 1·160 | 1·307 | 1·257 | 1·170 |
| Quotient N/P | 2·00 | 1·81 | 1·80 | 1·73 | 1·69 | 1·66 | 1·42 | 1·37 | 1·40 |
| Removed nitrogen, mgm. | 2·49 | 2·82 | 3·50 | 3·41 | 3·20 | 2·91 | 3·62 | 3·53 | 3·27 |
| Protein removed (as percentage of total protein) | 87 | 94 | 96 | 98 | 100 | 100 | Hydrolysis of T | | |
| Average per cent. | | 92% | | | 100% | | | | |
| Average N/P. | | 1·87 | | | 1·69 | | | 1·40 | |
| N/P of the lanthanum salt of T, treated with the same reagent during the identical times | | 1·69 | | | 1·68 | | | 1·37 | |

cent. protein solution were treated with 4 × 2 litres of Carnoy fluid (intensive grinding was necessary).   Total time for each treatment 5 minutes. The precipitate was separated on a suction filter, washed with alcohol, ether and petroleum ether, freezed solid with carbon dioxide and cut twice in slices 10 μ thick.   Washed with alcohol and dried *in vacuo* the powder contained 1·00 per cent. P and 13·53 per cent. N.   All other preparations with Carnoy of proteins and T were made in the same way.

About 30 mgm. of this preparation were treated with 10 c.c. of **Ma-La** at 30° with constant stirring and subsequent filtration, washing with absolute alcohol, and analysis (Table II.).

## TABLE IV.

| Before the treatment with Ma-La: | | | | | | |
|---|---|---|---|---|---|---|
| Protein-nitrogen, mgm. . | 1·11 | 1·31 | 1·04 | 1·17 | 1·14 | 1·31 |
| T-nitrogen, mgm. . . | 1·61 | 1·90 | 1·50 | 1·73 | 1·69 | 1·94 |
| Time of treatment, hours . | 1/2 | 1/2 | 4 | 4 | 21 | 21 |
| Percentage nitrogen removed | 86·5 | 87·0 | 100 | 98·3 | >100 | >100 |

## TABLE V.

| | Number of Experiment. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **1.** | | | **2.** | | | **3.** | | |
| | a. | b. | c. | a. | b. | c. | a. | b. | c. |
| **Weight of preparation, mgm.** | 30·2 | 31·4 | 31·3 | 33·6 | 32·0 | 35·0 | 33·1 | 30·4 | 32·3 |
| Phosphorus, mgm. . | 1·60 | 1·66 | 1·65 | 1·77 | 1·69 | 1·85 | 1·75 | 1·61 | 1·71 |
| Nitrogen, mgm. . | 5·67 | 5·90 | 5·88 | 6·31 | 6·01 | 6·57 | 6·88 | 5·71 | 6·07 |
| Protein nitrogen, mgm . . . | 2·98 | 3·10 | 3·09 | 3·31 | 3·16 | 3·45 | 3·26 | 3·00 | 3·18 |
| **Time of treatment, hours** . . | ½ | ½ | ½ | 4·0 | 4·0 | 4·0 | 20½ | 20½ | 20¼ |
| **Undissolved:** | | | | | | | | | |
| Nitrogen, mgm. . | 3·31 | 3·65 | 3·39 | 2·98 | 2·96 | 3·15 | 2·35 | 2·22 | 2·27 |
| Phosphorus, mgm. | 1·62 | 1·67 | 1·67 | 1·80 | 1·70 | 1·86 | 1·75 | 1·62 | 1·70 |
| Quotient N/P . | 2·04 | 2·18 | 2·03 | 1·67 | 1·74 | 1·69 | 1·34 | 1·37 | 1·34 |
| **Removed nitrogen mgm.** . . | 2·36 | 2·25 | 2·49 | 3·33 | 3·05 | 3·42 | 3·87 | 3·49 | 3·85 |
| Removed phosphorus, mgm . | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 |
| Removed protein (as percentage of total protein) . | 79 | 73 | 81 | 100 | 97 | 99 | Hydrolysis of T | | |
| Average protein removed (as percentage of total protein) . . | | 78% | | | 99% | | | | |
| **Average quotient N/P** . . . | | 2·08 | | | 1·70 | | | 1·35 | |
| Lanthanum salt of T + 10 c.c. of Ma-La; analysis of the undissolved N/P . . . | | 1·69 | | | 1·70 | | | 1·37 | 0·99 (44 hours) |

The removal of the protein was almost complete after half an hour.

Equivalent amounts (calculated for the values for sodium and $SO_4$) of T and histon sulphate (from *Thymus* : 14·11 per cent. N and 0·06 per cent. P) were mixed and allowed to remain in a shaking apparatus for twenty-four hours. The precipitation was washed many times with water in a centrifuge and dessicated with alcohol and ether. Treatment with Ma-La was as in experiment Table II.

In other experiments, carried out in the same way, but at another time and with another histon preparation, the following averages were obtained (Table IV.). No phosphorus was found in any of the solutions, and the total phosphorus in the solids was exactly the same as before the treatment. In theseexperiments the solids were quantitatively collected for analysis.

Histon, then, can be removed completely by Ma-La from its salt with nucleic acid. There is danger, however, of hydrolysis of the nucleic acid, which of course will be in the nature of splitting the purine bases off. At times up to at least one hour this danger can be disregarded.

Protamin sulphate from herring sperm, precipitated four times as a picrate and converted into the sulphate, contained (when dried *in vacuo* over $P_2O_5$ at room temperature) 21·68 per cent. N.

Equivalent amounts of this sulphate and T (with regard to $SO_4$ and sodium) were mixed, shaken two hours, centrifuged and washed until free from $SO_4$ with water in the centrifuge. The thread-shaped precipitate was dried in the usual way. 5·75 per cent. P ; 18·77 per cent. N ; N/P = 3·26. Steudel found [3] a quotient N/P in spermatozoon heads = 3·24 and in a synthetic product, like ours = 3·21. In Table V. another preparation was used with the values 18·77 per cent. N ; 5·28 per cent. P. It was treated in the same way as the preparations in Tables II., III. and IV.

The results with protamin, are similar to those with histon in Tables III. and IV.

As to the important question about the solubility and stability of the lanthanum-salt of T.

(b) The possibility of precipitating protein free from nucleic acid, has only been tried in a few experiments, carried out in exactly the same way as those given in Table I.

| *Zinc-formalin reagent :* | (a) | Buffer, diluted | . | . | . | . | 50 | c.c. |
|---|---|---|---|---|---|---|---|---|
| | | Formalin | . | . | . | . | 50 | ,, |
| | | Zinc acetate 1 molar | . | . | . | 15 | ,, |
| | | Water | . | . | . | . | . | 99·1 | ,, |
| | | | | | | | 214·1 | ,, |
| | (b) | Buffer, conc. | . | . | . | . | 9·1 | ,, |
| | | Formalin | . | . | . | . | 100 | ,, |
| | | Zinc acetate 1 molar | . | . | . | 15 | ,, |
| | | | | | | | 124·1 | ,, |
| *Buffer-composition ;* *Diluted :* | | Sodium acetate $N/1$ | . | . | . | 148 | ,, |
| | | Acetic acid $N/1$ | . | . | . | . | 34 | ,, |
| | | Water | . | . | . | . | . | 818 | ,, |
| | | | | | | | 1000 | ,, |

*Buffer concentrated :* without distilled water.

The formalin was made from a preparation containing 34 per cent. $CH_2O$ and about 16 per cent. $CH_3OH$, in the following way :—

| | |
|---|---|
| Formalin (kept under pure nitrogen) . . | 450·0 c.c. |
| Sodium hydrate $N/1$ . . . . | 18·0 ,, |
| HCOONa $N/1$ . . . . . . | 13·0 ,, |
| Water . . . . . . . | 19·0 ,, |
| | 500·0 ,, |

$p_H$ about 7·5.

The reagents (a) and (b) were saturated with sodium chloride immediately before use. 25 c.c. were poured into about 2 gr. of solution, containing T and protein (see Table I.), each weighed in the form of solutions. As will be seen from Table VI., only the reagent (a) is suitable for precipitating the protein quantitatively, whereas the nucleic acid in all cases is almost quantitatively left in the solution. No experiments have as yet been performed to test these reagents on already precipitated proteins and nucleic acid.

TABLE VI.

| | Number of Experiment. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1. | | 2. | | 3. | | 4. | |
| | *a.* | *b.* | *a.* | *b.* | *a.* | *b.* | *a.* | *b.* |
| **Before precipitation:** | | | | | | | | |
| Total protein nitrogen, mgm. . . | 1·19 | 1·17 | 3·11 | 3·07 | 5·91 | 5·48 | 7·69 | 8·03 |
| Total nucleic acid nitrogen, mgm. . | 2·04 | 2·01 | 1·65 | 1·62 | 1·24 | 1·16 | 0·68 | 0·70 |
| **In the precipitate :** | | | | | | | | |
| Total nitrogen, mgm. | 1·38 | 0·44 ? | 3·37 | 2·47 | 6·04 | 5·29 | 7·52 | 7·63 |
| Nucleic acid nitrogen mgm.. . . | 0·017 | 0·017 | 0·019 | 0·097 | 0·097 | 0·079 | 0·091 | 0·065 |
| Nucleic acid nitrogen (as percentage of the total nitrogen in the precipitate) | 1·2 | — | 0·6 | 3·9 | 1·6 | 1·5 | 1·2 | 0·9 |

The precipitates were allowed to stand an hour before filtration and washing. On account of the large amounts of sodium chloride the values for phosphorus are not very reliable. Colorimetric methods are unsatisfactory, when unusual amounts of mineral salts are present, and in these experiments the $P$ had to be determined by such a method,[7] because it was present in extremely small amounts.

### 2. Proteolytic Enzymes + Lanthanum Acetate.

The purpose of these experiments has already been set forth in the introduction.

### Preparations.

The enzyme was made according to the method of Waldschmidt-Leitz. The glycerin extract did not lose more than 25 per cent. of its activity (after activation), when stored for a month at $+ 2°$, and had an

activity of 12-7 "trypsin units" on casein, calculated for 1 c.c. extract made with 87 per cent. glycerine. The enterokinase was prepared according to a modification of the usual method.[8] 1 gr. of desiccated mucous membrane from the upper parts of the intestine was shaken for three hours at 30° with 50 c.c. water + 4 drops $N/10$ NaOH. After centrifuging, the fluid was mixed with 5 c.c. $N/1$ acetic acid per 100 c.c. of the solution. The precipitate was filtered off after 1½ hours (30°), and neutralised with $N/1$ NaOH against litmus-paper whilst vigorously stirring. The solution is water-clear and colourless (just as the glycerin extract from desiccated pancreas), but somewhat unstable (25 per cent. loss after 12 hours by + 2°), and is almost immediately destroyed by alkali. It contains about 0·08 mg. $N$ and 0·02 mg. $P$ per 1 c.c. The activated trypsin was prepared when required, by mixing 1 part of enterokinase solution and 1 part of glycerin extract from pancreas diluted (with water 1/10). After thirty minutes at 30° the solution was ready for use. Table VII. shows the influence of enterokinase on the activation (6 per cent. casein solution).

TABLE VII.

TABLE VIII.

| Glycerin Extract. c.c. | Enterokinase Solution. c.c. | Water. c.c. | Trypsin Units. |
|---|---|---|---|
| 1 | 0·1 | 1·9 | 6·6 |
| 1 | 0·3 | 1·7 | 7·1 |
| 1 | 0·5 | 1·5 | 8·2 |
| 1 | 1·0 | 1·0 | 9·0 |
| 1 | 2·0 | 0·0 | 9·0 |

| Time in Hours. | Trypsin Units. |
|---|---|
| 0 by 30° | 8·2 |
| 13 ,, ,, | 8·2 |
| 67 ,, ,, | 8·8 |
| 192 ,, ,, | 7·9 |
| 336 ,, + 2° | 5·4 |

The stability of an activated solution is comparatively good at 30°.

As a rule, therefore, we have used activated extracts which have been standing at 30° over night. The determinations of trypsin units were always performed according to Waldschmidt-Leitz.[9] We will use the following abbreviations for the different reagents :—

At = 2 parts activated trypsin solution + 1 part water.

At-La = 2 parts activated trypsin solution + 8 parts water + a part $M/5$ lanthanum acetate. The reagent must be left for one hour and then filtered from a small precipitation. This precipitate has been investigated, as it is of some importance. It contains about 4·8 per cent. $N$ and 4 per cent. $P$. The weight obtained from 5 c.c. At is 17·9 mgm. We imagine it consists of lanthanum phosphate and lanthanum-nucleic-acid-protein. The precipitate was always removed before the actual experiments, and in this way the enzyme preparation was always to all practical purposes free from phosphorus.

At-La-Bf = 2 parts of activated trypsin solution + 5 parts water + 2 parts $N/1$ NH$_4$Cl + 1 part $N/50$ NH$_3$ + a parts $M/5$ lanthanum acetate. (Filtration as in the case of At-La).

At-La and At-La-Bf have also been used at higher concentrations.

At-La conc. = 2 parts activated trypsin solution + 3 parts water + a parts $M/5$ lanthanum acetate.

In some experiments no water at all was added (Table IX., series XXIV., preparation C).

[8] Waldschmidt-Leitz, *Z. physiol. Chem.*, **142**, 217, 1925 ; Waldschmidt-Leitz, *Z. physiol. Chem.*, **125**, 150, 1923; E. Widmark, *Upsala, personal communication, unpublished.*

[9] R. Willstätter, E. Waldschmidt-Leitz, S. Dañaiturria, *Z. f. physiol. Chem.*, **161**, 209, 1926.

**At-La-Bf conc.** = 2 parts activated trypsin solution + 2 parts $N/1$ $NH_4Cl$ + a parts $N/50$ $H_3$ + 1 part $M/5$ lanthanum acetate.
The quantity of **a** has varied between 0·25 and 0·02 c.c.
**At-Bf** = At-(La)-Bf without **a**.

**The following are some Essential Properties of these Reagents:**

10 c.c. **At-La-Bf** ($a = $ 0·25) + 5 c.c. 6 per cent. casein.  30°.

| Time in min. | 20 | 50 | 120 | 300 |
|---|---|---|---|---|
| c.c. $N/5$ KOH consumed | 0·51 | 1·08 | 1·71 | 2·41 |

2·46 c.c. At + 2·54 c.c. Bf + 5 c.c 6 per cent. casein, 30°.

| | | | |
|---|---|---|---|
| $p_H$ (glass electrode) | 7·54 | 8·29 | 9·56 |
| c.c. $N/5$ KOH consumed after 20 min.. | 0·80 | 0·76 | 0·89 |

In the literature maximal digestion is said to be given at $p_H = $ 8·7, but for our purposes it seems to be of small importance, even if the $p_H$ varies between 7 and 9.

10 c.c. **At-La-Bf** + 5 c.c. 6 per cent. casein.

| | 20° | 30° |
|---|---|---|
| Temperature | | |
| c.c. $N/5$ KOH consumed | 0·54 | 0·86 |

The retardating action of lanthanum ions is indicated by the following figures :—

10 c.c. **At-La-Bf** + 5 c.c. 6 per cent. casein, 20 min., 30°.

| (a) c.c. | 0·00 | 0·10 | 0·20 | 0·25 | 0·50 | 1·00 |
|---|---|---|---|---|---|---|
| Trypsin units | 8·0 | 5·8 | 5·1 | 4·7 | 1·3 | 0·2 |

On account of the comparatively strong retardation we never used more than 0·25 c.c. lanthanum acetate + 10 c.c. of the other ingredients.

The retardation was reproduceable as is shown by the following figures :—

| | | | | |
|---|---|---|---|---|
| a = 0, trypsin units | 8·0 | 6·5 | 10·6 | 9·7 |
| a = 0·25, trypsin units | 4·7 | 3·4 | 5·9 | 6·0 |
| Retardation in percentage of the values for $a = $ 0 | 41 | 42 | 44 | 38 |

The above experiment was made with **At-La-Bf.**
The effect of retardation without buffer is shown below :—

2 c.c. activated trypsin solution + 8 c.c. water + a c.c. lanthanum acetate.

| a c.c. | 0·0 | 0·125 | 0·25 |
|---|---|---|---|
| Trypsin units | 8·6 | 6·7 | 3·9 |
| Retardation in percentage | — | 23 | 55 |

The same enzyme preparation in the form of **At-Bf** gave 9·7 trypsin units. The absence of buffer involves a retardation of about 9 per cent.
The values for trypsin units have been calculated from the equation :
$$\frac{\text{c.c. KOH} \times 10}{1·05} = \text{trypsin units.}$$ Three titrations were made for each determination, and three blanks for each of the series. The figures are averages. The error by one titration may be up to 0·1 c.c. $N/5$ KOH.

In Table IX. are given the results of experiments upon the phosphorus splitting power of the enzyme. Such experiments were in all cases made on new pancreas-enterokinase preparations and always with the same result, *viz.*, that our enzyme-preparation contained no active polynucleotidases. Tests containing three c.c. At (8·8 trypsin-units) + 5 c.c. T were left to react at 30°. After intervals 2 c.c. were withdrawn, mixed with 0·1 c.c. protein solution and precipitated with 2 c.c. 10 per cent. trichloracetic acid, filtered after 2 minutes, and analysed with the help of the " Stufen " colorimeter.[7]

It was, moreover, ascertained too, that under the experimental conditions, trichloracetic acid did not split off any phosphorus from T. It must be remembered that the enzyme preparations in these experiments had not been freed from inorganic phosphorus by lanthanum acetate. The same experiment was repeated in the presence of a buffer, lanthanum acetate, with enterokinase alone, and with concentrated reagents. In no instance was an increase of the inorganic phosphorus observed. On the contrary, the lanthanum salt of the nucleic acid always removed a very small but definite amount of phosphorus from the enzyme solution.

TABLE IX.

| Time in Hours. | μgm. (o·oo1 mgm.) Inorganic Phosphorus in Filtrate [from Calculated Nuclei. Acid Phosphorus (*n*) in Test, μgm. | | |
|---|---|---|---|
| | *n.* o. | *n.* 664. | *n.* 3320. |
| o (about 5 min.) | 110 | 104 | 105 |
| ⅓ | 118 | 118 | 124 |
| 6 | 109 | 141 | 126 |
| 48 | 121 | — | 131 |

It is of great importance for our purpose to know the solubility of the lanthanum nucleinate under different conditions. As far as determinations of phosphorus can be trusted, there seems to be no solubility to take into account. As our purpose is to render the nucleic acid in microscopical structures insoluble, while removing the proteins, it was thought advisable to examine the solubility of the lanthanum salt by other methods.

Nucleic acid exhibits an intensive absorption in the ultraviolet (Fig. 8A). The specific absorption about the wave-length 2600 Å.U. depends essentially on the purine and pyrimidine groups in the molecule.

As this absorption is very strong, it is possible to carry out quantitative determinations upon extremely small quantities with the ultraviolet spectrograph. It is also possible to determine the lanthanum contents of a solution in this way, as lanthanum has no specific absorption in the extreme ultraviolet.

The lanthanum nucleinate was prepared as follows : 50 c.c. of a 1 per cent. solution of the sodium salt of nucleic acid were added drop by drop to 50 c.c. of $M/10$ lanthanum acetate + 200 c.c. buffer, $p_H = 3.77$ (7 c.c. $N/1$ sodium acetate + 48 c.c. $N/1$ acetic acid + 145 c.c. water), whilst stirring. The round bubbles formed were broken up with a glass rod, the whole shaken for twenty-five hours, the precipitate carefully crushed and shaken again with the mother liquor for twenty-four hours. The precipitate was washed with alcohol and petroleum ether and dried *in vacuo* at room temperature [7·37 per cent. P]; 25 mg. of lanthanum nucleinate were shaken for twenty-four hours with lanthanum acetate of various concentrations (Table X.). Then the undissolved substance was filtered off, and the absorption spectrum of the clear liquid was determined with a Zeiss quartz spectrograph. (The following equipment was used : Tungsten arc, rotating sector 1/10 and Hüfner rhombus, Cornu-prism, camera *f*. 600 mm.)

A series of spectrograms was taken, corresponding to different thicknesses of the absorbing layer. These are then matched with the simultaneously recorded comparison-spectra with the aid of a microscope in the usual manner. The extinction-coefficients of the matching points were then determined with the aid of the following formula :

$$\epsilon = \frac{1}{d} \cdot \log \frac{I}{I_0} ;$$

where $d$ represents the thickness of the absorbing layer in cm., and $I/I_0$ is 1/10 (*cf*. above).

In this manner there was recorded the absorption spectrum of a series of solutions of nucleic acid and lanthanum acetate within the range of molar concentrations from $0.25 \times 10^{-4}$ to $0.50 \times 10^{-6}$ and $1.6 \times 10^{-2}$ to $0.4 \times 10^{-3}$, and the extinction coefficients were thus calculated with
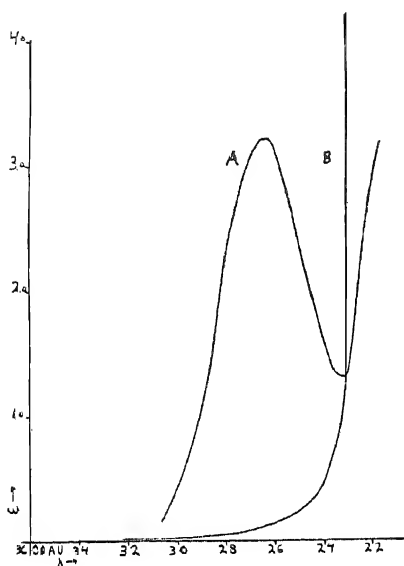


FIG. 8.
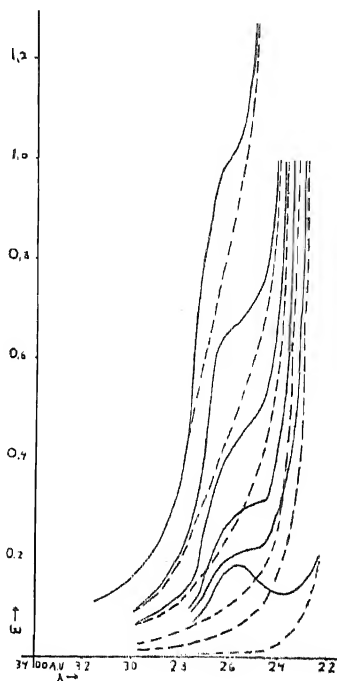


FIG. 9.

great accuracy.   Only the absorption curves are given in Fig. 8.   Both substances followed Beer's law exactly.

Fig. 9 shows the absorption spectra of the solutions which are in equili-

TABLE X.—MOLAR LA-CONCEN-
TRATION OF THE SOLUTIONS
(PREVIOUS TO THE ADDITION
OF THE NUCLEINATE).

| A | $16 \cdot 10^{-3}$ mols. La-Ac$_3$ |
|---|---|
| B | 8 ,, |
| C | 4 ,, |
| D | 1·6 ,, |
| E | 0·8 ,, |
| F | 0·4 ,, |
| G | 0·08 ,, |
| H | 0·0 ,, |



FIG. 10.

brium with the solid lanthanum nucleinate at different La concentrations (Table X.).

To determine the amount of nucleic acid in the solutions it is necessary to subtract the absorptions of the lanthanum in the solution.   At the higher La-concentrations the La, corresponding to the La-nucleinate,

may be neglected. At the lower concentrations, however, this cannot be done, but it is possible to determine the amount of La from the absorption on both sides of the absorption maximum in a most simp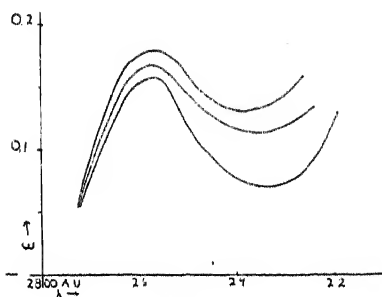le way. This correction has been introduced into the curves in Fig. 9. The lanthanum absorptions are marked with dotted lines in Fig. 9.

Fig. 10 shows the difference curves, which thus represent the absorption of the nucleic acid in the solution in dissociated and undissociated state. With increasing La-concentration, the curve drops, corresponding to a diminution of the solubility. The smallness of this effect, however, makes the more exact calculation of the solubility product impossible. Further difficulties would arise through the complicated dissociation conditions.

With increasing concentration of La the solubility is not much affected. This may depend either on the fact that at an extremely low La-concentration the nucleinate in solution exists almost exclusively as undissociated molecules, or on the fact that in the nucleinate preparation a minute amount of purines in directly soluble form may be present as decomposition products of the rather unstable nucleic acid. If the effect were due to this last factor, the solubility stated below would be yet several times lower.

With these reservations the conditions in the solution are defined through the content of absorbing nucleic acid.

From Fig. 10 we may calculate that under the given conditions solid lanthanum nucleinate is in equilibrium with a solution of nucleic acid of the molar strength $0.55 \times 10^{-5}$ or about 0.0009 per cent. The difference in the absorption about 2200-2500 Å.U. makes a determination of the lanthanum content possible. This is about $10^{-4}$ mol. With a ten times higher La-concentration, the concentration of the nucleic acid is depreciated by about 1/10. The discrepance between the La- and the nucleic acid concentrations depends on the fact that it seems to be impossible to prepare a La-nucleinate absolutely free from adsorbed lanthanum.

Further investigations at yet lower La-concentrations are of no practical interest, and it is impossible to get a numeral value of the solubility product because of the complications introduced by the dissociation conditions and the instability of the substance.

The solubility of the lanthanum nucleinate is extremely low. Already at a lanthanum concentration of $10^{-4}$ mols. the amount of nucleic acid in the solution is less than 0.001 per cent.

Previous analyses had shown that nucleic acid is split by the **Ma-La-**reagent. Therefore the following investigation was carried out in order to determine the velocity of the reaction.

0.1 g. nucleic acid was treated at 30° C. for varying times with 20 c.c **Ma-La.**

Nitrogen and phsophorus determinations were carried out on both the undissolved substance and on the clear fluid. On the latter also the ultraviolet absorption spectrum was recorded. The determinations of phosphorus in the fluid, although negative, are of little value, because lanthanum phosphate is almost insoluble. The quantitative determinations showed a continuous decomposition of the nucleic acid accompanied by a fall in the quotient $N/P$ in the undissolved substance immediately after the beginning, when it consists of undecomposed lanthanum nucleinate 1.69.

| After | 1 hour's exposition the quotient was — | 1.68 |
|-------|----------------------------------------|------|
| ,, | 4 hours' ,, ,, ,, | — 1.60 |
| ,, 20 ,, | ,, ,, ,, | — 1.37 |
| ,, 44 ,, | ,, ,, ,, | — 0.99 |

These figures show that during one hour no noticeable decomposition of the nucleic acid has occurred under the conditions of the experiment.

Among the decomposition products of the nucleic acid, purine bases are very likely to be found, as they are very soon split off by acid hydrolysis. By ultraviolet spectrography it is possible to determine concentrations

of these bases, below 0·001 per cent. and it ought therefore, to be possible to show an incipient decomposition very readily. The spectrograms of the reaction fluids showed, however, no such increasing specific absorption, indicating, either that there were no purines among the decomposition products or that they were themselves decomposed immediately after liberation. Special experiments showed that the **Ma-La-**reagent very rapidly decomposed free purine bases, which speaks strongly in favour of the latter hypothesis.

The solubility of the lanthanum salt in other buffers than ammonia - ammonium chloride may be considerable : 0·04 gr. lanthanum salt (1·11 mg. nitrogen) + 10 c.c. phosphate buffer (Sörensen) were shaken during twenty hours at 30°.

### TABLE XI.

| $p_H$ in the fluid . | 7·0 | 7·2 | 7·4 | 7·6 |
|---|---|---|---|---|
| Nitrogen, mgm. in the fluid . | 0·81 | 0·58 | 0·52 | 0·67 |

The same experiment in borate-HCl-buffer (Sörensen) :

### TABLE XII.

| $p_H$ in the fluid . | 7·6 | 7·8 | 8·0 | 8·2 | 8·4 | 8·6 | 8·8 | 9·0 |
|---|---|---|---|---|---|---|---|---|
| Nitrogen, mgm. in the fluid . . | 0·09 | 0·11 | 0·17 | 0·29 | 0·27 | 0·33 | 0·34 | 0·80 |

The same experiment was made with ammonia-ammonium chloride buffer. No phosphorus was found, after combustion, by the colorimetric method, between $p_H$ 6·85 and 9·20.

Freshly prepared lanthanum salt was shaken with different fluids and weighed after drying *in vacuo* to constant weight at 20° (Table XIII.).

### TABLE XIII.

| Fluid. | Weight of Lanthanum Salt (a). Mgm. | Time of Reaction in Hours. | Weight of Lanthanum Salt after Reaction (b). Mgm. | Weight Decrease. Per Cent. of (a). |
|---|---|---|---|---|
| (A) Water ; 10 c.c. . . | 22·1 | 15 | 22·4 | 0 |
| (B) $M/200$ lanthanum acetate ; 10 c.c. . | 24·3 | 15 | 24·8 | 0 |
| (C) Water ; 3·8 c.c. + glycerine ; 0·2 c.c. + $N/1$ $NH_4Cl$ ; 4 c.c. + $N/50$ $NH_3$ ; 2 c.c. | 35·6 | 15 | 33·3 | 5 |
| (D) Water ; 3·55 c.c. + $M/5$ lanthanum acetate ; 0·25 c.c. + glycerine ; 0·2 c.c. + $N/1$ $NH_4Cl$ ; 4 c.c. + $N/50$ $NH_3$ ; 2 c.c. | 31·0 | 24 | 31·3 | 0 |

When lanthanum salt is not present a very small portion was dissolved (C). Other experiments were carried out in the same way with **At conc.** (E.) ; **At-La conc.** (F) ; **At-Bf conc.** (G) ; **At-La-Bf conc.** (H).

The weight decreases (percentage) of *a* were :

| E. | F. | G. | H. |
|---|---|---|---|
| 8·5 | 0·0 | 15·7 | 4·4 |

With lanthanum in the solution practically no substance was dissolved. Determinations of the phosphorus in the fluids supported this result, although the solubility product of lanthanum phosphate was found to be very low (for the neutral salt = 6·2 × 10⁻⁸ at 30°), which rather diminishes the value of determinations of this nature.

10 mgm. T in solid form were digested with **At-La-Bf conc.** (a = 0·25) during twenty-four hours at 30°:

Phosphorus in the solution before digestion 0·085 mgm.
,,             ,,          ,,    after       ,,       0·084  ,,

The same experiment with a solution of **T** :

Before digestion 0·065 mgm. *P.*
After          ,,     0·069     ,,

The amount of lanthanum acetate (0·25 mgm./10 c.c.) is sufficient.

The digestive power of the enzyme on histon and protamin : 2 c.c At (8·5 trypsin units) + solutions + 5 c.c. 1 per cent. protamin sulphate, twenty minutes at 30° ; titration with $N/5$ KOH (Table XIV.).

TABLE XIV.

| Solutions. | Lanthanum Acetate. $M/5$. | $N/5$ KOH. |
|---|---|---|
| 2 c.c. $N/1$ NH₄Cl + 1 c.c. $N/50$ NH₃  .    . | 0·25 c.c. | 0·37 |
| ,,          ,, | 0·00 c.c. | 0·35 |
| Water, 3 c.c.    . | 0·25 c.c. | 0·32 |
| ,,          ,, | 0·00 c.c. | 0·36 |

TABLE XV.

| Lanthanum Acetate. c.c., $M/5$. | $N/5$ KOH. c.c. |
|---|---|
| 0·0 | 0·55 |
| 0·06 | 0·40 |
| 0·25 | 0·40 |

With an assumed molecular weight of 5000 (?) the amount of protamin was 1 × 10⁻⁵ mols. and the consumed KOH was 7 × 10⁻⁵ mols.

The blanks gave a heavy precipitate with alcohol, and it is not possible therefore to give any zero figures. The digested tests, however, gave no precipitates on titration. The figures in the table show that lanthanum had no retarding action.

Histon sulphate was precipitated with NaOH, washed and digested : it dissolved completely. 2 c.c. activated trypsin solution (6·8 trypsin units) + 3 c.c water + 10 c.c. 1 per cent. histon sulphate ($p_H$ = 7), twenty minutes at 30°, titration with $N/5$ KOH (Table XV.).

Blanks could not be carried out. Lanthanum acetate had very small retarding effect. With an assumed molecular weight of 10,000 (?) the amount of histon would have been 1 × 10⁻⁵ mols. and that of KOH was 10-8 × 10⁻⁵.

## Preparations of Protein and T for Enzyme Digestion.

Various amounts of solutions of protein and **T** were weighed, mixed and treated as follows :—

(*A.*) Mixed with **La-Bf,** precipitate washed with the reagent, with alcohol and ether, dried *in vacuo* at room temperature.

(*B.*) *Serum* + **T.** Treated with Carnoy (p. 3, Table II.) during forty minutes, washed with alcohol, extracted in Soxhlet with alcohol

during ten hours, ground in a mortar and dried *in vacuo* at room temperature.

(1) Treated further with lanthanum acetate in sodium acetate-acetic acid buffer of $p_H = 4.74$, heated for ten minutes at 100°, washed with alcohol and dried *in vacuo* at room temperature.

(2) Part of No. 1 was frozen with $CO_2$ and cut ($5\mu$) four times, washed with alcohol and ether and dried *in vacuo* at room temperature.

(C.) Treated with Carnoy five minutes, washed with alcohol, cut twice ($5\mu$), washed with alcohol and ether and dried *in vacuo* at room temperature.

(D) Precipitated with alcohol and :

(1) Heated to 90° and afterwards treated with **La-Bf**, used for digestion directly without drying.

(2) Washed with alcohol and ether and dried *in vacuo* at room temperature.

(E) Equivalent amounts of protamin sulphate and T were mixed. All of the T and protamin was precipitated.

(F) Histon sulphate and T as in (E). Of the different preparations $F_4$ contained the purest histon (free from slimy substance and giving—as sulphate—an absolutely clear and colourless solution). It was controlled so that all the T was precipitated.

It was necessary before determining the nitrogen, in all experiments, where ammonium buffer was used, to drive off the ammonia, without decomposing protein and the bases in T. This was carried out in an apparatus, composed entirely of glass, in which the ammonia was distilled (eventually determined quantitatively) at reduced pressure with steam. Different alkaline buffers were used, and the difficult determinations were checked by careful controls.

### Digestion-Experiments.

The preparations were kept (when not otherwise mentioned) in centrifuge tubes at 30° in constant movement together with the enzyme-preparations (usually = 10 c.c.). These were changed from time to time, and after each period the remaining solids were quantitatively filtered off. The precipitates were washed with a diluted solution of lanthanum acetate in water. Analysis was made on the undissolved matter + filtra, on the solutions (usually collected) or on both. Usually the concentration of the lanthanum acetate was decreased from the first digestion to the third. In each table the amounts of lanthanum acetate are stated as c.c. $M/5$-solution (the value $a$), and the digestion times in hours. All values are averages of three determinations. Table XVI. : **At-La-Bf** **conc.** $a = 0.25$. Digestion times : 2·5, 18, 30.

TABLE XVI.*

| Column. | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. | 11. | 12. | 13. | 14. | 15. | 16. | 17. | 18. | 19. | 20. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Prepara-tions. | Nitrogen, Amount in Enzyme Solution. Mgm. | | | | Nitrogen, Amount in Digestion-Solution. Mgm. | | | | Nitrogen Increase in Solution. | Analysis of Solid Preparations, before Digestion. Mgm. | | | | | Undissolved N, mgm. | N decrease in Un-dissolved. | Average of Cols. 9 and 16. | Per cent. Digestion (Col. 17). | Undissolved + Dig. Solut. N mgm. | N in Preparation + N in Enzyme. |
| | 1st Change. | 2nd Change. | 3rd Change. | Σ | 1st Change. | 2nd Change. | 3rd Change. | Σ | | Weight mgm. | P mgm. | N mgm. | Nucleic Acid-N mgm. | Protein N, mgm. | | | | | | |
| A 1 | 1·19 | 1·21 | 2·12 | 4·52 | 1·38 | 1·42 | 4·21 | 7·01 | 2·49 | 29·8 | 0·75 | 3·78 | 1·27 | 2·51 | 1·46 | 2·32 | 2·40 | 96 | 8·42 | 8·30 |
| A 2 | 1·19 | 1·21 | 2·12 | 4·52 | 1·93 | 1·63 | 4·25 | 7·81 | 3·29 | 29·7 | 0·63 | 4·14 | 1·06 | 3·08 | 1·03 | 3·11 | 3·20 | 100 | 8·84 | 8·66 |
| A 3 | 1·19 | 1·21 | 1·27 | 3·67 | 1·38 | 2·05 | 2·36 | 5·79 | 2·12 | 29·1 | 0·77 | 4·20 | 1·30 | 2·90 | 2·15 | 2·05 | 2·09 | 72 | 7·94 | 7·87 |
| A 4 | 1·19 | 1·21 | 1·27 | 3·67 | 1·47 | 1·62 | 3·22 | 6·31 | 2·64 | 29·7 | 0·67 | 4·56 | 1·12 | 3·44 | 1·79 | 2·77 | 2·70 | 78 | 8·10 | 8·23 |
| A 5 | 1·19 | 1·21 | 2·12 | 4·52 | 1·38 | 1·56 | 4·19 | 7·08 | 2·56 | 31·0 | 0·66 | 3·92 | 1·12 | 2·80 | 1·46 | 2·46 | 2·51 | 90 | 8·54 | 8·44 |
| A 6 | 1·19 | 1·21 | 1·27 | 3·67 | 1·40 | 1·63 | 3·48 | 6·51 | 2·84 | 29·8 | 0·61 | 4·25 | 1·04 | 3·21 | 1·48 | 2·77 | 2·80 | 87 | 7·99 | 7·92 |

* The agreement between the values in cols. 19 and 20 serves as a control on the accuracy of the determinations.

TABLE XVII.*

| 1. Series | II | | III | IV | | V | VI | VII | |
|---|---|---|---|---|---|---|---|---|---|
| 2. Preparation | $A_1$ | $A_4$ | $A_1$ | $A_1$ | $A_4$ | $B_1$ | $B_1$ | $B_1$ | $B_1$ |
| 3. Weight, mgm. | 61·5 | 62·4 | 31·4 | 61·4 | 62·1 | 63·6 | 60·0 | 30·4 | 30·2 |
| 4. Nitrogen, mgm. | 7·63 | 7·91 | 3·90 | 7·72 | 7·87 | 8·17 | 7·70 | 3·90 | 3·88 |
| 5. Phosphorus, mgm. | 1·913 | 0·595 | 0·98 | 1·91 | 0·61 | 2·47 | 2·33 | 1·18 | 1·17 |
| 6. Protein nitrogen, mgm. | 4·40 | 6·91 | 2·24 | 4·39 | 6·84 | 4·00 | 3·76 | 1·91 | 1·90 |
| **Examination of Undissolved Matter :** | | | | | | | (Weight of solid 8·3 mgm.) | (Weight of solid 9·9 mgm.) | |
| 7. Nitrogen, mgm. | 5·36 | 2·37 | 2·66 | 1·20 | 0·61 | 9·0 | 0·59 | 1·12 | 0·00 |
| 8. Phosphorus, mgm. | 1·925 | 0·541 | 1·01 | 0·57 | 0·21 | 2·54 | 0·637 | 0·60 | 0·00 |
| 9. Removed protein nitrogen, mgm. | 2·27 | 5·54 | 1·24 | T also dissolved ! | | 0 | T also dissolved ! | | |
| 10. Percentage protein-digestion | 52 | 80 | 55 | | | 0 | | | |
| **Examination of Solutions :** | | | | First 5 changes : 11·0  Sixth change : 2·50 | 11·0  2·50 | | | | |
| 11. Nitrogen in enzyme solution, mgm. | 3·25 | 3·35 | 4·29 | | | 9·66 | — | — | — |
| 12. Phosphorus in enzyme solution, mgm. | 0·00 | 0·00 | 0·00 | First 5 changes : 2·05  Sixth change : 0·63 | 2·05  0·63 | 0·58 | — | 0·77 | — |
| 13. Nitrogen in solution after digestion, mgm. | 5·52 | 8·78 | 5·59 | First 5 changes : 12·20  Sixth change : 7·60 | 13·50  7·00 | 9·66 | — | — | — |
| 14. Phosphorus in solution after digestion, mgm. | 0·00 | 0·00 | 0·00 | First 5 changes : 1·56  Sixth change : 2·50 | 2·50  — | 0·50 | — | 1·56 | — |
| 15. Increase of nitrogen, mgm. in solution | 2·17 | 5·43 | 1·30 | First 5 changes : 1·20  Sixth change : 5·10 | 2·50  4·50 | 0·00 | — | — | — |

TABLE XVII. (*cont.*).

| Series | II. | | III. | IV. | | V. | VI. | VII. | |
|---|---|---|---|---|---|---|---|---|---|
| Preparation | A₁. | A₄. | A₁. | A₁. | A₄. | B₁. | B₁. | B₁. | B₁. |
| 16. Percentage digestion calculated from column 15 | 49 | 79·5 | 58 | First 5 changes: 27 — | First 5 changes: 37 — | — | — | — | — |
| 17. Average of 10 and 16 | 51 | 80 | 56·5 | — | — | 0 | — | — | — |
| 18. Trypsin - units in enzyme (At) | 8·5 | 8·5 | 8·9 | 8·0 | 8·0 | 8·1 | 7·6 | 9·2 | 9·2 |
| 19. N/P in the preparation (No. 2) | 4·0 | 13·0 | 4·0 | 4·0 | 13·0 | 3·3 | 3·3 | 3·3 | 3·3 |
| 20. N/P in the undissolved matter (Nos. 7-8) | 2·78 | 4·38 | 2·63 | — | — | — | 0·93 | 1·86 | — |

\* Series II. **At-La-Bf.** Three changes : 0·25, 0·125, 0·063. Dialysation times : 27, 21, 22 hours. The sum of the nitrogen in preparation and enzyme was for A₁ = 10·88 and that of the nitrogen in undissolved and digestion fluid was 10·88. The same figures for A₄ were 11·26 and 11·15.

Series III. **At-La-Bf:** Weight of preparation half of that in Series II. Five changes. a = 0·25, 0·20, 0·15, 0·10, 0·05. Digestion times 5 × 20 hours.

Series IV. **At-La-Bf.** Six changes. The first five are the same as in Series III. The sixth without lanthanum acetate. T was dissolved, and it is obvious, that it must always be protected by lanthanum acetate in the solution. The low digestion in the first changes probably depends on the surface of the preparation being aged and not large enough. (Two months older than in Series II. and III.).

Series V. **At-La-Bf conc:** five changes with 20 c.c. enzyme solution in each. a = 0·25, 0·20, 0·15, 0·10, 0·05. Reaction times, 4 × 2 hours and 26 hours. No digestion!

Series VI. **At-Bf conc.** 20 c.c. Digestion time, 24 hours. T dissolved.

Series VII. **At-La-Bf conc.** 20 c.c. enzyme. a = 0·08, 0·04, 0·02. Digestion times, 11, 13, 24 hours ; 94 per cent. protein and 49 per cent. T dissolved.

The Series V.-VII. show, that the fixation and protein are of great importance. In all of them serum was used and heat-lanthanum fixation. The preparations were old and contained hard particles. They could be digested though, when the lanthanum concentration was very low, but then T would go into solution.

As the following experiments are made with the same method, we have tried to arrange them in Tables XVIII.-XX. to which reference should be made.

TABLE XVIII.

SERIES VIII.-XI.: At-La. SERIES XII. At-La MORE CONCENTRATED [5 (2 C.C. ACTIVATED TRYPSIN SOLUTION + a C.C. LANTHANUM ACETATE)].

| 1. | 2. | VIII. | | | IX. | | | | | XI. | XII. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Series. | | | | | | | D₁. | | For each of these Experiments Two Equal Portions of Protein—T Solution were Precipitated with Alcohol, Centrifuged and, without washing, One Digested, the Other Analysed (4.7). | |
| | Preparation. | B₂ | | | C | | | | | | |
| 3. | Weight, mgm. | 31·3 29·9 | 29·5 | 25·3 | 28·0 | 23·5 | 22·1 24·4 23·6 | | | 5·93 8·80 10·99 / 5·78 8·67 10·72 | 5·78 8·67 10·72 |
| 4. | Nitrogen mgm. | 4·41 4·21 | 4·16 | 4·01 3·62 | 3·37 | 4·26 4·70 | 4·55 | 5·82 8·52 10·71 | 5·14 5·87 6·42 | 2·40 1·37 4·28 | 2·44 1·40 0·667 |
| 5. | Phosphorus, mgm. | 1·30 1·24 | 1·23 | 1·34 1·21 | 1·13 | 0·40 0·44 | 0·42 | 2·40 1·37 0·653 | | 6·02 1·93 4·55 | 1·91 4·73 8·17 |
| 6. | N/P | 3·39 3·39 | 3·39 | 2·99 2·99 | 2·99 | 10·76 10·76 | 10·76 | 2·43 6·22 16·40 | | 0·658 2·43 | 1·65 6·27 9·60 |
| 7. | Protein-nitrogen, mgm. | 2·21 2·11 | 2·08 | 1·74 1·57 | 1·46 | 3·58 3·95 | 3·82 | 1·74 6·19 9·60 | | 9·87 1·65 6·27 | |
| | **Undissolved Matter:** | | | | | | | | | | |
| 8. | Nitrogen, mgm. | 3·59 3·27 | 2·87 | 3·32 2·74 | 0·23 | 2·51 1·29 | 0·25 | 5·14 5·87 6·42 | | 3·96 4·68 6·41 | 4·67 6·63 5·45 |
| 9. | Phosphorus, mgm. | 1·26 1·23 | 1·24 | 1·36 1·25 | — | 0·46 0·43 | — | 2·40 1·37 0·655 | | 0·658 2·43 1·41 | 2·44 1·40 0·666 0·667 |
| 10. | N/P | 2·85 2·74 | 2·31 | 2·44 2·19 | — | 5·45 3·00 | — | 2·14 4·28 9·80 | | 6·02 1·93 4·55 | 1·91 4·73 8·17 |
| 11. | Removed protein-nitrogen, per cent. | 0·82 0·94 | 1·29 | 0·69 0·88 | — | 1·75 3·41 | — | 0·68 2·65 4·29 | | 1·10 2·26 | 1·11 2·04 5·45 |
| 12. | Digestion per cent. | 37 45 | 62 | 40 56 | (>100) | 49 86 (>100) | | 39 43 45 | | 76 34 / 71 67 36 / 23 20 | 57 / 67 33 57 |
| 13. | a | 0·40 0·25 0·10 / 0·20 0·10 0·05 / 0·10 0·063 0·04 | 0·10 0·06 0·04 | 0·20 0·10 0·05 / 0·10 0·05 0·025 / 0·05 0·025 0·013 | 0·05 0·025 0·013 | 0·20 0·10 0·05 / 0·10 0·05 0·025 / 0·05 0·025 0·013 | 0·05 0·013 0·013 | 0·25 0·25 0·25 / 0·05 0·05 0·05 / — | | 0·125 0·125 0·125 / 0·063 0·063 0·063 / 0·031 0·031 0·031 | 0·25 / 0·125 / 0·063 / 0·031 |
| 14. | Digestion times in hours. | 17 17 / 12 12 / 11 11 | 17 12 11 | 17 17 / 9 9 / 15 15 | 17 9 15 | 17 17 / 9 9 / 15 15 | 17 9 15 | 23 23 / 15 15 / — | | 23 20 / 15 12 / — | 20 / 12 / 12 |
| 15. | Trypsin-units of At. | 9·1 | | 8·8 | | 8·8 | | 7·2 | | 7·6 | 7·3 |

TABLE XIX.—At-La CONC. 10 C.C. IN EACH CHANGE.

| 1. Series | XIII. | XIV. | XV. | XVI. | XVII. | XVIII. |
|---|---|---|---|---|---|---|
| 2. Preparations | $D_2$ | $D_2$ | E. | $F_1$ | $F_2$ | $F_8$ |
| 3. Weight in mgm. | Precipitated as in Series XI. and XII. in Table XVIII. | 8·74  8·74  8·74  10·86  10·86  10·86 | 39·8  42·5 | 39·7  31·2  45·7 | 40·9  40·3  32·1 | 33·7  32·9  34·0 |
| 4. Nitrogen, mgm. | 5·78  8·67  10·72 | 6·29  6·29  6·29  16·50  16·50  16·50 | 7·48  7·99 | 6·31  4·96  7·26 | 6·48  6·38  5·08 | 5·44  5·31  5·48 |
| 5. Phosphorus, us, mgm. | 2·43  1·41  0·662 | 1·39  1·39  1·39  0·658  0·658  0·658 | 2·29  2·44 | 1·21  0·95  1·39 | 1·31  1·29  0·995 | 1·20  1·17  1·21 |
| 6. N/P | 2·38  6·15  16·19 | 6·29  6·29  6·29  16·50  16·50  16·50 | 3·26  3·26 | 5·21  5·21  5·21 | 4·97  4·97  4·97 | 4·52  4·52  4·52 |
| 7. Protein nitrogen, mgm. | 1·65  6·27  9·60 | 6·39  6·39  6·39  9·75  9·75  9·75 | 3·59  3·88 | 4·26  3·35  4·91 | 4·27  4·21  3·35 | 3·40  3·32  3·43 |
| **Undissolved Matter:** | | | | | | |
| 8. Nitrogen, mgm. | — — — | 5·64  4·07  2·40  3·64  0·99 | 3·69  4·25 | 4·07  3·00  5·07 | 4·81  4·27  0·23 | 4·19  3·44  0·35 |
| 9. Phosphorus, mgm | — — — | 1·45  1·39  1·21  0·676  0·444 | 2·366  2·50 | 1·19  0·95  1·33 | 1·31  1·31  0·07 | 1·22  1·18  — |
| 10. N/P | — — — | 3·89  2·95  1·98  5·38  2·23 | 1·56  1·70 | 3·42  3·16  3·81 | 3·67  3·26  — | 3·43  2·91  — |
| 11. Removed protein nitrogen mgm. | — | 3·10  4·67  6·04  7·22  9·51 | 3·79  3·74 | 2·24  1·96  2·17 | 1·67  2·11  4·85 | 1·25  1·87  5·17 |
| 12. Digestion, percentage | All dissolved | 49  73  95  74  98  All dissolved | 100  96 | 53  59  44 | 39  50 Solution | 37  56 Solution |
| 13. a c.c. in changes | 0·063  0·047  0·023 | 0·14  0·10  0·07  0·06  0·033<br>0·07  0·05  0·033  0·05  0·033<br>0·033  0·025  0·025  0·025  0·025 | 0·25  0·25<br>Preparation on filter. 40 c.c. dropped during 20 hours through preparation. | 0·25  0·25  0·25<br>0·125  0·125  0·125<br>0·03  0·063  0·063 | 0·20  0·10  0·05<br>0·10  0·05  0·025<br>0·04  0·02  0·01 | 0·25  0·125  0·06<br>0·125  0·06  0·03<br>0·063  0·03  0·015 |
| 14. Times of digestion in hours | 12  12  12 | 12  12  12  12  12  12<br>6  6  6  6  6  6<br>17  17  17  17  17 | 20  20 | 15  15  15<br>10  10  10<br>14  14  14 | 15  15  15<br>7  7  7<br>9  9  9 | 14  14  14<br>11  11  11<br>12  12  12 |
| 15. Trypsin-units of At | 8·3 | 6·4 | 7·5 | 7·0 | 8·1 | 6·8 |

TABLE XX.

| 1. Series | XIX. | XX. | XXI. | XXII. | XXIII. | XXIV. |
|---|---|---|---|---|---|---|
| 2. Preparation | "Nucleo-Histon": Precipitation from Thymus Extract with Acetic Acid, dried with Alcohol. | "Nucleohiston." | "Nucleohiston." | "Nucleohiston." | Protein-T digested with Ma-La (Table II.) | C. |
| 3. Weight in mgm. | 62·9 77·9 53·9 | 55·9 55·7 56·0 66·0 | 67·9 69·1 70·6 72·2 | 70·7 68·8 66·8 63·7 | 50·5 78·4 | 34·1 34·3 34·0 34·0 |
| 4. Nitrogen, mgm. | 9·62 11·91 8·24 | 8·55 8·52 8·56 10·09 | 10·38 10·56 10·79 11·04 | — — — — | 7·03 10·91 | 4·62 4·64 4·61 4·61 |
| 5. Phosphorus mgm. | 1·56 1·93 1·34 | 1·34 1·33 1·34 1·58 | 1·62 1·65 1·69 1·73 | — — — — | 3·26 5·06 | 0·341 0·343 0·340 0·340 |
| 6. N/P | 6·39 6·39 6·39 | 6·39 6·39 6·39 6·39 | 6·39 6·39 6·39 6·39 | — — — — | 2·16 2·16 | 13·53 13·53 13·53 13·53 |
| 7. Protein nitrogen, mgm. | 6·98 8·65 5·98 | 6·20 6·19 6·30 7·42 | 7·54 7·67 7·94 8·12 | — — — — | 1·49 2·32 | 4·04 4·06 4·03 4·03 |
| Undissolved Matter: | | | | | | |
| 8. Nitrogen, mgm. | 5·92 5·37 0·80 | 5·36 1·20 — — | 9·07 9·19 0·87 — | — — — — | 6·78 10·57 | 1·17 0·70 0·66 0·64 |
| 9. Phosphorus mgm. | 1·54 1·80 0·20 | 1·72 0·53 — — | 1·86 1·74 0·344 — | — — — — | 3·25 5·06 | 0·360 0·339 0·365 0·355 |
| 10. N/P | 3·84 2·98 — | 3·12 — — — | 4·87 5·28 — — | — — — — | 2·09 2·09 | 3·25 2·06 1·81 1·80 |
| 11. Removed protein nitrogen, mgm. | 3·70 6·32 8·04 | 3·19 7·32 — — | 1·31 1·37 — — | — — — — | 0·25 0·34 | 3·45 3·94 3·95 3·97 |
| 12. Digestion percentage. | 53 73 Dis-solution | 51 Solution | 17 18 Solution | Solution | 17 15 | 85 97 98 99 |
| 13. a c.c. | 0·25 0·12 0·06 / 0·12 0·06 0·03 / 0·06 0·03 0·02 | 0·20 0·07 0·02 0·007 / 0·10 0·035 — — / 0·05 0·018 — — | 0·15 0·05 0·015 — / 0·075 0·025 0·0075 — / 0·038 0·013 0·0038 — | 0·03 0·015 0·008 0·004 / — — — — / — — — — | 0·25 0·25 As in Table XIX. Series XV. E | 0·12 0·08 0·07 0·25 Preparations had been digested 3 times with pepsin before this digestion! / 0·06 0·07 0·06 / 0·03 0·02 0·02 |
| 14. Digestion times in hours | 17 17 17 / 9 9 9 / 15 15 15 | 11 11 11 11 / 11 11 — — / 14 14 — — | 11 11 11 11 / 11 11 11 — / 14 14 14 — | 10 10 10 10 / — — — — / — — — — | 20 20 / — — / — — | 12 12 12 12 / 12 12 12 12 / 12 12 12 12 |
| 15. "Preventing" salts in enzyme solution | At-La conc. | At with CeCl₃ instead of La (ac)₃ | At with Al₂(SO₄)₃ instead of La (ac)₃ | At with Th(SO₄)₂ instead of La(ac)₃ | At-La conc. | No water added to At-La |
| 16. Trypsin-units of At | 7·0 | 6·8 | 6·8 | 7·2 | 7·5 | 12·0 |

Somewhat extensive experiments were also made with pepsin-lanthanum digestion. They do not seem to be of interest at present and are therefore not recorded here.

For the purpose of removing protein by means of proteolytic enzymes, leaving a structure of lanthanum nucleinate undissolved, it is necessary that lanthanum ions should be present in the solution. When the amount of lanthanum acetate is 0·1 c.c. of a $M/5$ solution in the first change, the highest digestion values are obtained. Protein can be eliminated in that way, but histon cannot be thus quantitatively removed. That can, however, be done by the Ma-La reagent. The digestion times must be long (a variation of some hours, therefore, is of no importance) and three changes are necessary. As we had very good results with a constant flow of enzyme solution (Table XIX., ser. XV., E. and Table XX., ser. XXIII.), a chamber has been constructed by Caspersson, which will enable him to digest sections of tissues under microscopical observation at different wave-lengths. The constant flow of enzyme solution is provided by a syringe, which is emptied by means of a special clockwork device in 1 : 6 or twenty-four hours.

We have digested cells (*Stenobotrus*) and have been able to show, that the chromosomes are rendered beautifully visible, in ordinary light, when mitotic cells were digested with At-La. The work on cells, which will maybe show something of interest, will be carried on by Caspersson, when the coming of the new lighting apparatus will permit an analysis of the chromosomes.

## GENERAL DISCUSSION.

**Miss D. M. Wrinch** (*Oxford*) said : The developments foreshadowed in the paper contributed by T. Casperson, E. Hammarsten and H. Hammarsten are likely to prove a landmark in our knowledge of Mitosis.

Already there exists a considerable body of data of a cytological nature with regard to the behaviour of chromosomes during Mitosis. There also exists the vast and formidable system of genetical facts. So far, however, fundamental theories as to chromosome structure which would allow the correlation of the cytological facts into one scheme are lacking and there has been no serious attempt, *i.e.* no attempt based upon the present state of knowledge of organic molecules—to relate the system of genetics (which is essentially a *closed* system) to current concepts in physical chemistry.

Recent developments in protein chemistry and in the X-ray analysis of aggregates of organic molecules make quite plain the nature of the concepts which such theories would have to employ, but direct evidence, which would enable us to attribute some degree of plausibility to one *schema* rather than another, has so far been of an extremely meagre nature.[1] The obvious procedure of applying to chromosomes the methods which have yielded information about other biologically less important organic molecules, and so attacking the problem from the start on fundamental lines, must wait upon developments of technique which may easily take decades.

If, therefore, our colleagues in Stockholm are able to give us information as to the varying distributions of proteins and nucleic acid during the mitotic cycle, we should welcome it with open arms as giving data which are very urgently required.

[1] A notable exception is the work of K. Linderstrøm-Lang on Clupein (see p. 326).

# METAPHOSPHORIC ACID AND PROTEINS.

By R. K. SCHOFIELD.

## The Titration of Ionisable Amino Groups in Proteins.

When proteins are titrated electrometrically with acid, indications are frequently obtained of an "end point" near to $p_H$ 2. If at this $p_H$ all the carboxyl groups are unionised, the amount of acid which reacts when a pure isoelectric protein is brought to this end point is equivalent to the number of ionisable amino groups.* This is true regardless of whether we think in terms of the older ideas or of the zwitterion theory, as can easily be seen by considering the general case in which there are $x$ carboxyl groups and $y$ amino groups. The isoelectric condition being that in which the number of positively charged groups exactly equals the negatively charged ones, we may use the symbol $a$ for the number of groups of either kind that are ionised before the introduction of the acid. The amount of acid which reacts is, therefore, the sum of the amount needed to convert the unionised amino groups into ions and of that needed to convert the $COO^-$ groups into $COOH$ groups. This is $(y - a) + a = y$, so that the amount of acid which reacts is a direct measure of the number of amino groups capable of ionisation.

The determination of this amount of acid by electrometric titration is, however, beset by difficulties of two kinds. First, since the instrumental readings vary as the logarithm of the concentration, uncertainties of a millivolt in the readings lead to errors of many per cent. in final values. Secondly, there is a theoretical difficulty in deciding what effect the presence of the protein has on the activity coefficient of the acid. The disturbance is due to the fact that the anions, which are taken up when proteins react with the common mineral acids, are held in a loose state of binding conditioned mainly by the necessity for electrical neutrality, and are free to take part in thermal movement.

The loosely bound condition of these anions is also, according to the Proctor-Wilson theory, the cause of the peptising action which dilute acids frequently exert. This peptisation makes difficult the general application of an alternative method in which an aliquot of solution containing some of the surplus acid, but free from protein, has to be separated by filtration or other means and back titrated. Even when the practical difficulties of separation can be overcome, there still remains the theoretical difficulty that, owing to the influence of the loosely bound anions on its activity coefficient, the acid left in contact with the protein will tend to be less concentrated than that extracted in the filtrate.

Both the drawbacks to the second method would disappear, if an acid could be found having anions which become firmly bound to the amino groups. Such an acid would be expected to be a powerful co-agulent, so that the separation of an aliquot free from protein should present no difficulties. Anions of such an acid, having become bound to

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* This term is used to cover all the nitrogen groups in the protein which are capable of becoming positively charged by co-ordinating a hydrion.

the protein and therefore being unable to execute independent thermal movement, should not influence the activity coefficient of the remaining acid.

We may even anticipate a further advantage from the use of such an acid, because an additional force would come into play, tending to make the reaction go to completion. If sufficient acid is present for practically every amino ion to become bound to an acid anion, an amount of acid equivalent to the amino groups will be carried out of solution even if not all the carboxyl groups are undissociated. For if any COO⁻ groups should remain, an equivalent number of H· ions must be carried down in order to preserve the electrical neutrality of the precipitate.

## Metaphosphoric Acid.

J. J. Berzelius [1] discovered, more than a century ago, that meta-phosphoric acid (glacial phosphoric acid) has the property, not shared by either the pyro- or the ordinary (ortho-) acid, of coagulating white of egg. After many years, this work was extended by R. Lorenz [2] who found that gelatine is similarly coagulated and that some metaphosphoric acid is carried down with the precipitate.

Although a few further studies have been made using other proteins, none appear to have been directed towards the estimation of amino-groups; yet it will at once be apparent that the use of metaphosphoric acid would remove the practical difficulty of separating a protein-free aliquot. There is also the argument, based on the Proctor-Wilson theory that such a coagulation indicates a firm binding of the acid anions by the protein. It is nevertheless a matter of interest to examine the system in more detail in order to see whether other grounds can be found for believing that the amino groups of proteins can bind metaphosphate ions more firmly than the anions of other mineral acids.

The structure and reactions of metaphosphoric acid strongly suggest that the binding is of the nature of a co-ordination. The electronic structure of the mono-acid together with the change involved in its hydrolysis to the ortho-acid may be represented thus :—
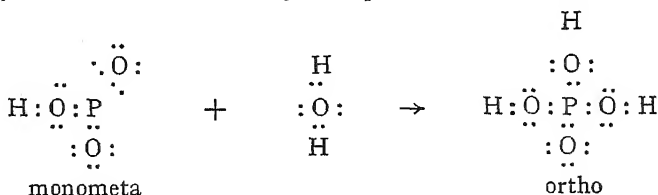


By the co-ordination of a fourth oxygen previously forming part of a water molecule the highly stable arrangement of four oxygens tetra-hedrally disposed about a central phosphorus is formed. The existence of monomidophosphoric acid which may be represented thus :—
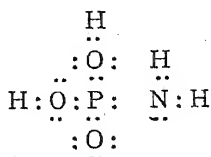
[1] J. J. Berzelius, *Gilbert's Ann.*, **53**, 393, 1816 ; **54**, 31, 1816.
[2] R. Lorenz, *Pflüger's Arch.*, **47**, 189, 1890.

shows that one of the oxygens may be replaced by a nitrogen. W. Schlömann[3] obtained precipitates when a concentrated solution of metaphosphoric acid is run into an etherial or alcoholic solution of primary amines. Thus an affinity clearly exists between metaphosphoric acid and amino groups.

The author, therefore, puts forward the hypothesis that the nitrogen atom of an ionised amino group in a protein can become associated with the three oxygens of a metaphosphate ion in forming a tetrahedral arrangement about the phosphorus atom. No other simple mineral acid is reported as sharing with metaphosphoric acid the power to coagulate white of egg, and this hypothesis accounts for the uniqueness of its position.

Nitric acid has the same structure but is stable, $H_3NO_3$ being unknown, while the pentoxides of the remaining elements of group five are either insufficiently soluble, or not acidic enough, or do not give clearly defined meta and ortho acids. Metaphosphorus acid, $HPO_2$, combines with water to form orthophosphorus acid, $H_3PO_3$, but does so with such rapidity that it is impossible to obtain $HPO_2$ in solution. $H_3NO_3$ is unknown, while solutions of $As_2O_3$ and $Sb_2O_3$ are only feebly acidic and sparingly soluble. The oxyacids of the elements in the earlier groups are all weak. $SO_3$ and $SO_2$ have the necessary structure but are not themselves acids, while $H_2SO_4$ and $H_2SO_3$ have fully saturated oxygen groups. The same is generally true of the oxyhalogen acids, except that $HIO_3$ forms acid salts in which four oxygens may be grouped about one iodine atom ; no evidence has, however, been obtained that two distinct forms, meta and ortho, can be obtained in solution.

## The Polymers of Metaphosphoric Acid.

Metaphosphoric acid has a marked tendency towards molecular association, and although this property does not appear to have been discussed hitherto from the standpoint of co-ordination, it would seem that two molecules of $HPO_3$ might be linked up in either of two ways, thus :—



(i)                                    (ii)
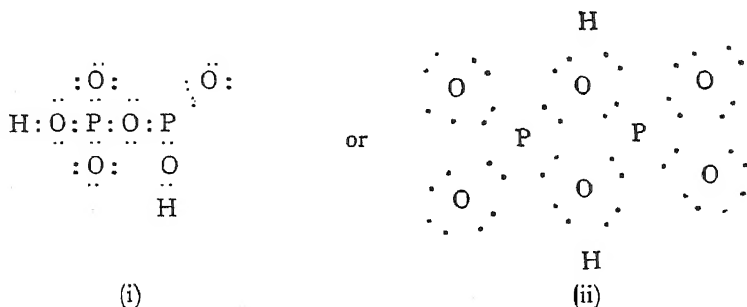
In (i) one of the phosphorus atoms has only three oxygens and so this molecule might, like the mono-acid, link up with an amino group. In (ii) both have complete four groups, so that a molecule of this kind should not on the hypothesis advanced be capable of linking up. The possible molecular configurations increase rapidly with the degree of polymerisation, but they may all be divided between those which have one phosphorus atom with only three oxygens about it, and those in

[3] W. Schlömann, *Ber.*, **26**, 1020, 1893.

which all the phosphorus atoms have complete groups of four. It would certainly be remarkable if no molecules of the second class exist so that our theory indicates that the power to coagulate white of egg should not be possessed by all metaphosphoric acids, but only by a particular group.

This idea is not necessarily at variance with the work of Balareff[4] and of Réchid[5] who found that the coagulating power increased with increase in the temperature to which the acid is subjected in the course of its preparation. For, although these authors were disposed to ascribe the effect to an increase in the degree of polymerization, there may at the same time have been an increase in the proportion of molecules of type (i). That polymerization is not in itself the important factor in coagulation is indicated by earlier work of Pascal[6] in which monometa phosphoric acid prepared from the ethyl ester caused immediate precipitation of egg-white. Our hypothesis, it should be noted, necessarily leads to the conclusion that the mono-acid should be active.

### Shift of the Isoelectric Point.

If the postulated binding between active metaphosphate ions and the amino ions of a protein is strong enough to resist disruption under the action of electrodialysis, the addition of such metaphosphate ions will, in effect, shift the isoelectric point of the protein towards the acid side. In other words, it will tend to suppress the amphoteric character of the protein and cause it to become more like a body with only an electronegative nature.

Mr. L. W. Samuel is carrying out a series of experiments under the author's direction with a view both to testing the hypothesis outlined above and to evolving a simple routine procedure for estimating ionisable amino groups in proteins. The results to date are most encouraging and have shed new light on the molecular complexity of metaphosphoric acid. We prefer, however, to reserve further comment until the present series of experiments is finished.

### Summary.

1. When a quantity of isolectric protein is brought into contact with an excess of a strong acid in dilute solution a certain quantity of the acid reacts with the protein. If a sufficient excess of acid is present to cause substantially all the carboxyl groups to be unionised, the quantity which reacts is equivalent to the ionisable amino group.

2. A difficulty arises in estimating the number of ionisable amino groups by this method, when the common mineral acids are used ; because the anions of the combined acid, being free to execute thermal movements, affect the activity coefficient of the residual acid. This disturbance should be absent when metaphosphoric acid is used, since, judging by their coagulating action, metaphosphate ions become firmly bound to the amino ions of the protein. The coagulation also makes the separation of an aliquot for back titration a simple matter.

3. The hypothesis is advanced that a metaphosphate ion condenses with an ionised amino group through the nitrogen atom's association with the three oxygens to form a tetrahedral group about the phosphorus atom.

This hypothesis explains why metaphosphoric acid alone among the mineral acids has been found to coagulate white of egg. It also indicates

[4] D. Balareff, *Z. Anal. Chem.*, **73**, 411, 1928.
[5] Réchid, *C.R.*, **196**, 860, 1933.
[6] P. Pascal, *Bull. Soc. Chim.*, **33**, 1611, 1923.

that among the many different kinds of metaphosphoric acid molecules that can be built up by the polymerisation of $HPO_3$ only a particular group should have this coagulating power.

*Soil Physics Department,*
*Rothamsted Experimental Station,*
*Harpenden.*

## GENERAL DISCUSSION.

**Dr. R. K. Schofield** (*Rothamsted*), in outlining the scope of his paper, said that his first idea was the essentially practical one, that in using an acid which coagulates the protein an aliquot can readily be separated for back titration, and in this way a determination can very easily be made of the acid taken up by the protein. Using this method, Mr. Samuel had found significant variations in the ratio $\frac{acid\ uptake}{N\ content}$ between a number of wheat flours which, if they turn out to reflect nothing more than the gliadin/glutenin ratio, are likely to be of value because the determinations are so simple. The $p_H$ used was about 1·5, and the absence of the difficulties already referred to in the discussion, which occur when using hydrochloric acid is to be attributed to the simultaneous closing down of both kinds of active group, the negative by combination with hydrogen ions and the positive by condensation with metaphosphate ions.

The hypothesis outlined to account for the specific behaviour of metaphosphoric acid seemed to be borne out by further experiments the results of which he hoped would be published quite soon. These experiments provide evidence that an ordinary metaphosphoric acid solution contains several kinds of anions, some of which are more strongly bound to proteins than others, and that there is a general correspondence between their firmness of binding and their rate of hydrolysis to orthophosphoric acid. It seems very likely that in the case of the mixed acid with which we are dealing, the anions that are most strongly bound include some polymers, and a question that is engaging our attention at the moment is whether a positive group is able to bind a whole polymerised ion or only one equivalent of it.

**Dr. D. Jordan Lloyd** (*London*) said : The method of titrating a protein with an acid which is also a precipitating agent has so many obvious advantages that it is surprising that it has not been thought of before. It will be of the greatest interest to see a number of proteins titrated with metaphosphoric acid and the titration curves compared with the standard curves obtained with hydrochloric acid. It should be of particular importance not only to obtain curves for the soluble proteins like the albumins and the gliadins, but also for the insoluble proteins like the collagens and the keratins.

**Dr. E. B. R. Prideaux** (*Nottingham*) inquired whether any care had been taken to prepare a pure metaphosphoric acid : as ordinarily prepared it was a mixture of several polymers with simple molecules. From esters, a pure metaphosphate could be prepared.

**Dr. R. K. Schofield,** in replying to Dr. Prideaux, thanked him for raising the point, saying that he was aware of these methods for preparing specific acids. Having first in mind the development of a practical method he and Mr. Samuel had set out to see how far the ordinary (and therefore cheap) acid could be turned to account.

# PART II. (E) OTHER SUBSTANCES.

## COLLOIDAL IONS OF STARCH.

By M. Samec.

### Historical.

Starch suspended or dissolved in water has a negative electric charge. This effect was first observed by A. Coehn [1] and other authors tested it on different starch solutions. F. Bottazzi and C. Victorow [2] worked, *e.g.*, with a starch which was heated on a waterbath with 60 per cent. potash, then precipitated with alcohol and freed from alkali by dialysis. Z. Grużewska [3] discovered the anodic migration of the amylopectin fraction of potato starch, and E. Fouard [4] observed the same ultramicroscopically, on ultra-filtered starch solutions with the apparatus of Cotton and Mouton.

According to F. Botazzi, C. Victorow and Z. Grużewska the negative electric charge can be exactly observed only on the amylopectin fraction, whilst the amyloses evidently do not migrate with decrease of potential. The origin of the electric charge remained meanwhile inexplicable.
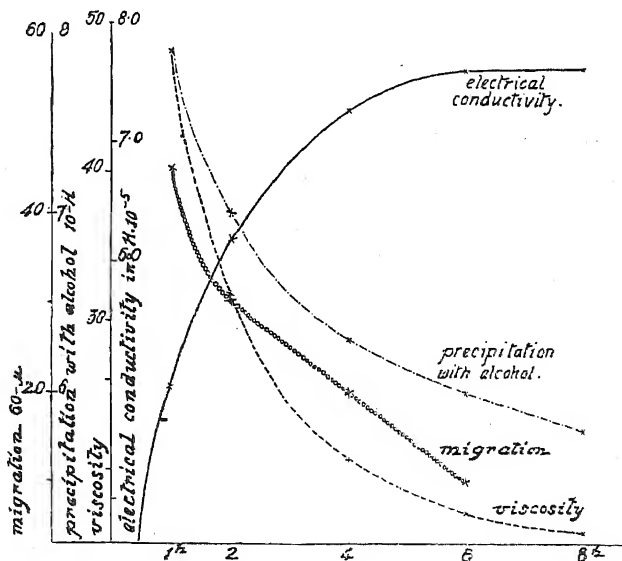


Fig. 1.

The first impetus to research on the present-day theory of starch ions was my observation that the electric migration of starch decreases when starch

[1] A. Coehn, *Z. Elektrochemie,* 4, 63, 1897.
[2] F. Bottazzi and C. Victorow, *Atti della reale academia dei Lincei* (5), 19, II, 7, 1910.
[3] Z. Gručewska, *Jo. physiol. path. gén.,* 14, 7, 1912.
[4] E. Fouard, *L'etat colloidale de l'amidon et sa constitution physikochimique* (Laval 1911), p. 9.

solution is heated under pressure.[5] The experiments were carried out as follows :—

A 2 per cent. solution of the purest potato starch was heated at 120° C in a gilded vessel of nickel in the autoclave and after different times of heating the electric migration was measured in the apparatus of Landsteiner-Pauli. At the same time we determined the specific conductivity of the solution. If $M$ signifies the time in minutes which is necessary to test starch with iodine in this apparatus with 220 volts in the anode tube, $K$ the specific conductivity and $t$ the time of heating in hours one obtains the diagram of Fig. 1.

The similarity of the change of the conductivity and migration indicated that, on heating with water, an electrolyte is liberated, which was initially attached to the starch and gave it the electric charge.

It was known from various researches that potato starch contains phosphates which cannot be removed by washing with water or with dilute acids.[6] Acids dissolve the cations, but change the quantity of phosphoric acid only slightly.[7, 8] On the other hand starch solutions, according to my observations lose a part of their phosphoric acid if they are completely dialysed. The longer the starch solution was heated under pressure the smaller was the quantity of undialysable phosphoric acid [9] (Table I.).

TABLE I.

| Period of heating at 120° C. : hours | 0 | 1 | 3 | 6 | 10 |
|---|---|---|---|---|---|
| Specific conductivity of the undialysed solution (2 per cent.) $K \times 10^{-5}$ . | 2·64 | 3·85 | 4·62 | 5·20 | 5·75 |
| Quantity of phosphoric acid after extreme dialysis : $P_2O_5$ per cent. | 0·168 | 0·159 | 0·095 | 0·035 | 0·011 |

From these determinations we see that the phosphoric acid combined in the starch has a decisive influence on the electrochemical behaviour of starch solutions.

## Constitution of Amylophosphoric Acid.

Three explanations might be given for the combination of phosphoric acid and polysaccharid :

(1) adsorption of phosphates ;
(2) formation of complexes after the theory by Werner ;
(3) esterification of the acid with the polysaccharid.

### (a) Adsorption Hypothesis.

Although I admit that starch dissolved in water adsorbs electrolytes, therefore also phosphates, I cannot agree with the opinion of some authors [10, 11] who postulate that the phosphoric acid which is present in natural starch and gives rise to the specific phenomena of the solutions is fixed by adsorption.

[5] M. Samec and F. von Hoefft, *Kolloidchem. Beih.*, **5**, 193, 1913.
[6] A. Fernbach, *Comptes rendus*, **138**, 428, 1904.
[7] E. Fouard, *Comptes rendus*, **144**, 501, 1907.
[8] H. Tryller, *Chem. Z.*, 44, 833, 1920.
[9] M. Samec, *Kolloidchem. Beih.*, **6**, 34, 1914.
[10] M. Schoen, *Bull. soc. Chem. Biol.*, **12**, 1033, 1930.
[11] J. Janicki, *Roczniki Chemji.*,**12**, 381, 1932.

Adsorption is a change of concentration between two limiting phases. It depends principally upon the surface tension and, consequently, there results, toward the interior of the solvent, a decrease of concentration. If the concentration in this phase is constantly low, the accumulation on the limiting phase must decrease.

Natural potato starch contains phosphoric acid chiefly in the form of acid potash salts. These salts are very soluble in water ; they cannot be insoluble infiltrates, despite the fact that they do not migrate (either from the starch grain or from the solution) on dialysis or electro-dialysis.

Commercial starches give cations on washing with acids, which form insoluble phosphates (e.g. Ca, Mg, etc.) without removal of phosphoric acid. This form of starch reacts equally with hydroxides or salts with the formation of Na- K- NH[4]- Mg- Ca-starches. The exchange takes place always between the cations, the phosphate ion remaining unchanged.[8]

By extreme electro-dialysis of starch solutions, hydrogen replaces the cations, but the phosphate ion remains intact. To explain this phenomenon by the hypothesis of adsorption one must assume that the phosphate ion is particularly well adsorbed whilst the cations are " normally " adsorbed. This assumption would not conflict with experience, for it is known that the anions of many salts can be adsorbed in greater measure than the cations. If there were an adsorbing tendency for phosphates colloidal starch solution must selectively adsorb phosphates present in solution, whereby an essential change of the colloidal properties could be noticed. Up to the present this has not been verified. The phenomenon of adsorption is further linked with the colloidal phase. If therefore starch is peptised or hydrolysed, its ability to bind phosphates must gradually diminish. We know, however, from the work of G. Malfitano [12] that starch when ultra-filtered through collodium is also combined with phosphorus.

By the hydrolysis of potato starch with diastase one can isolate products which contain more phosphoric acid than the starch. I have obtained for instance,[13]

Amylodextrin with 0·264 per cent. $P_2O_5$
Erythrodextrin with 0·338 per cent. $P_2O_5$
and　　　　Achrodextrin with 0·511 per cent. $P_2O_5$.

Similarly, H. Pringsheim [14] observed the retention of phosphorus on hydrolysis with pancreas extract.

The peptisation of potato starch with ultraviolet rays gives a product with 3·26 per cent. $P_2O_5$ ; [15] hydrolysis with hydrochloric acid gives substances with a low molecular weight [16, 17] of 7·7 to 12·73 per cent. $P_2O_5$. Recently T. Posternak isolated from potato starch a biose-phosphoric acid.[18] These experimental results cannot be explained on an absorption hypothesis.

[12] G. Malfitano, Comptes rendus, 143, 400, 1906.
[13] M. Samec, Kolloidchem. Beih., 6, 49, 1914.
[14] H. Pringsheim, H. Barchardt and R. Lewy, Naturwiss., 21, 299. 1933.
[15] M. Samec, Kolloidchemische Beih., 23, 377, 1926.
[16] J. Northrop and J. M. Nelson, J. Amer. Chem. Soc., 38, 472, 1916.
[17] M. Samec, Kolloidchem. Beih., 33, 449, 1931.
[18] T. Posternak, Comptes rendus, 197, 1157, 1933.

## (b) " Complex " Hypothesis.

G. Malfitano assumed that $(C_6H_{10}O_5)_x$ molecules are arranged like Werner complexes around a phosphate ion and that they are externally compensated by hydrogen, alkali or alkali earth ions.[19]   Such complexes of the first degree form complexes of higher degree, so that in general the constitution can be summed up as follows :—

$(\text{Ma})^{\pm} \, b_y \mp$ . . . . . complex of first degree
$[(\text{Ma b})_n(\text{Ma})]^{\pm} \, b_y +$ . . . . complex of second degree
$[(\text{Ma } b_y)_n(\text{Ma})b_y]_z(\text{Mab}_y)_n(\text{Ma})]^{\pm} \, b_y \mp$ . complex of third degree.
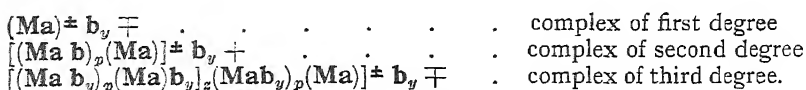
The complex would be therefore built up from an electrolyte **a-b** and a non-electrolyte **M** ; the ion **a** would be thereby entirely " dissimulated," the ion **b** partially so.[20]

This hypothesis however, cannot serve to explain the linkage of phosphoric acid in potato starch.   The isolation of the low molecular polysaccharid-phosphoric acids does not accord with it, for these decomposition products must consequently be assumed to have the constitution of a complex compound, which is contrary to modern ideas in organic chemistry.

The following views are of greater importance.[21]   According to the complex hypothesis the phosphate ions are entirely masked and the cations partially masked.   In the first degree complex the $PO_4$ ion could still act electrochemically, for the complex receives the charge of the $PO_4$. In the second degree complex however, 50 per cent., and in the third degree complex 66 per cent. of the cations are masked.   This conception does not however, apply in the case of potato starch, which has been studied with particular care.   When this starch is repeatedly washed with 1 per cent. hydrochloric acid, we find in 100 g. of dried substance $992 \times 10^{-5}$ equivalents of anions and only $62 \times 10^{-5}$ equivalents of cations.   Only 6 per cent. of the cations, which correspond to the acid are difficult to remove and not the 50 per cent. or 66 per cent. as the " complex " hypothesis would demand.

Purified potato starch, which has been washed with diluted hydrochloric acid or electrodialysed takes up alkali and seems to be neutral, if 1 gram atom of phosphorus corresponds to about 1·6 gram equivalents of the alkali.   This is approximately the quantity of alkali which is combined with *ortho*-phosphoric acid at the neutral point.   The hydrogen ions, also, are therefore not noticeably masked.

A further consequence of the " complex " binding of phorphoric acid is the postulate that phosphoric acid could be removed only by destruction of the micelles.   In this respect also the behaviour of starch does not agree, because it is possible to remove considerable quantities of phosphoric acid when the starch is boiled under pressure and the solution electro-dialysed, but the degree of dispersion is not noticeably changed.[21]

## (c) Esterification Hypothesis.

The ester hypothesis,[22] according to which amylophosphoric acid would be characterised by the group $R$—$O$—$PO_3H_2$, accords best with the facts.

This may be a dibasic acid which dissociates in aqueous solution with liberation of hydrogen ions and reacts with salts or alkalies.   We can

[19] G. Malfitano, *Comptes rendus*, 126, 1681, 1913.
[20] G. Malfitano, *Kolloid. Z.*, 46, 3, 1928.
[21] M. Samec, *Biochem. Z.*, 218, 249, 1930.

visualise on this hypothesis the retention of the phosphoric acid on washing starch with acids, the complete mobility of the cations, the accumulation of phosphorus on hydrolytic splitting of the polysaccharide residue **R**, the chemical reactivity of the unswollen starch grains and many other properties. On account of the great importance of carbohydrate phosphoric acid in enzymatic processes the appearance of such a grouping in carbohydrate-containing substances is well imaginable and, in fact, the ester hypothesis has been adopted by most authors.

The synthesis of starch phosphoric acids provides essential support for this hypothesis. It was thought that the presence of the ionogenic group $ROPO_3H_2$ must not only be a criterion of certain features of the electrochemical and chemical behaviour of starch, but must also influence the colloid-chemical behaviour. Micelles, which contain amylo-phosphoric acid possess more water on account of the ionic hydration, and lead therefore to more viscous solutions than the micelles of the free polysaccharide. We notice, indeed, on heating starch solutions under pressure, simultaneously with increase of the conductivity, a decrease of electric migration ; moreover, the undialysable phosphoric acid decreases, as well as the viscosity of the solution.[22, 23] Although the splitting-off of the phosphoric acid is not the sole cause of the decrease of the viscosity, it is a fundamental cause.[24, 25, 26, 27]

Starch may be very readily esterified by phosphorus oxychloride.[28, 29] On esterification not only does the quantity of undialysable phosphoric acid increase, but also the viscosity and the conductivity increase to a large extent, whilst the iodine coloration and the reducing power do not change noticeably (Table II.).[28]

TABLE II.

| | $P_2O_5$ Per Cent. | $10^5 \times K$ in 2 Per Cent. Solution. | $t/t_1$ in 1 Per Cent. Solution. | Iodine Coloration. | Reducing Power $R_m$. |
|---|---|---|---|---|---|
| Amyloses . . . | 0·00 | 0·2 | 1·008 | clear blue | 0·3 |
| Phosphoryl Amyloses . | 2·06 | 31·3 | 43·1 | ,, | 0·5 |
| Erythroamyloses . . | 0·00 | 0·52 | 1·16 | brown-violet | 1·26 |
| Phosphoryl Erythroamyloses . . | 2·19 | 29·2 | 17·7 | ,, | 1·21 |

The synthetic amylophosphoric acids are analogous to the natural starch fractions which contain amylophosphoric acid, in their acidic properties and in their electrochemical behaviour.

## The Isolation of the Starch Component Containing Phosphoric Acid.

It was of great importance to ascertain whether phosphoric acid in starch solutions is distributed homogeneously over the whole starch material or not.

[22] M. Samec and F. von Hoefft, *Kolloidchem. Beih.*, **5**, 141, 1913.
[23] M. Samec, *Kolloidchem. Beih.*, **6**, 23, 1914.
[24] See M. Samec, *Kolloidchemie der Stärke*, Dresden-Leipzig, 1927, p. 260 ff.
[25] M. Samec and A. Mayer, *Kolloidchem. Beih.*, **16**, 89, 1922.
[26] M. Samec, *Z. gesam. Getreide, Mühlen u. Bäckereiwesen*, **20**, 4, 1933.
[27] M. Samec, *Rocznik. Chem.*, **13**, 607, 1933.
[28] J. Kerb, *Biochem. Z.*, **100**, 3, 1919.
[29] M. Samec and A. Mayer, *Kolloidchem. Beih.*, **16**, 91, 1923.

Most researches on fractionation were based on the above-mentioned hypothesis, that amylophosphoric acid is more hydrated than the free polysaccharide. One had primarily, therefore, to ascertain the phosphoric component in the most viscous or gelled starch fractions.

Starch grains can be separated in various ways into a sol and a gel fraction. Following L. Maquenne the first fraction is usually named the amylose fraction, and the second the amylopectin fraction.

According to several authors the amylose fraction contains little or no phosphorus, whilst the amylopectin fraction contains nearly all the phosphorus of the starch grains (Table III.).

TABLE III.*—POTATO STARCH.

| Author. | Method of Fractionation. | $P_2O_5$ Per Cent. in | |
|---------|--------------------------|-----------|-------------|
| | | Amyloses. | Amylopectin. |
| M. Samec [9] . . | Formation of a paste with alkali, precipitation with $H_2SO_4$; dialysis . . . . | 0·007 | 0·185 |
| H. C. Sherman and J. C. Baker [31] . | Formation of a paste with hot water, centrifuging . . | 0·023 | 0·147 |
| M. E. Baldwin [32] . | Formation of the paste by freezing with water . . | 0·004- | 0·174 |
| M. Samec . . | Electro-dialysis of the solution . | 0·000 | 0·175 |

* The different distribution of phosphorus in the starch fractions is not confirmed by some authors. This is due to the experimental method employed. P. Karrer and E. von Krauss [33] treated the starch several times with hot water and compared the solved fractions. (Compare E. L. Hirst, M. T. Plant and M. D. Wilkinson.) [34]

Starch solution, which is prepared under pressure can be separated similarly. Electrodialysis is the best method, since the phosphoric fraction settles as a slimy phase on the bottom.[35, 36, 37] A sharp limit between the phases is attained, together with extreme purification. This electrodialytic separation succeeds only when the starch has not undergone considerable peptisation. Solutions of potato starch when heated for not more than three hours at 120° C. form two sharply limited phases, but on longer boiling or at higher temperatures one observes after electrodialysis that there are more liquid phases lying one over the other with feeble limits. The uppermost phase contains no phosphorus, whilst in the underlying phases the phosphorus content increases with the depth. Solutions of soluble starch and starch derivatives with still smaller micelles do not separate on electro-dialysis. In order to isolate the phosphoric component in such case one employs preferably precipitation with lead acetate or barium-hydroxide and alcohol [38] and removes the metal by forming an unsoluble salt.

[30] M. Samec, N. Minaeff and N. Ronžin, Kolloidchem. Beih., 19, 203, 1924.
[31] H. C. Sherman and J. C. Baker, J. Amer. Chem. Soc., 38, 1885, 1916.
[32] M. E. Baldwin, J. Amer. Chem. Soc., 52, 2907, 1930.
[33] P. Karrer und E. v. Krauss, Helv. chim. acta., 12, 1114, 1929.
[34] E. L. Hirst, M. M. Plant and M. D. Wilkinson, J. Chem. Soc., 54, 2375,1932.
[35] M. Samec and H. Haerdtl, Kolloidchem. Beih., 12, 281, 1919.
[36] M. Samec und A. Mayer, Kolloidchem. Beih., 13, 272, 1921.
[37] Ibid., 16, 89, 1922.        [38] M. Samec, Kolloidchem. Beih., 33, 449, 1931.

## The Size Range of the Amylophosphate-Ion.
### (a) Osmosis.

The determination of particle size of starch presents great difficulty. There is no exact method for the large, strongly hydrated charged micelles of amylophosphoric acid having hydrogen ions or metallic ions.

The amylophosphoric acid present in starch solutions which have been boiled for a short time, does not pass a collodion-membrane and one observes in such osmometric apparatus a temporary stable pressure, which is not reproducible. For the following reasons it is difficult to explain this :—

1. The solution contains hydrogenic or metallic ions, whose effect upon the osmotic pressure is unknown.

2. The observed pressure is not in linear proportion with the concentration of the solution.

As to (1), if the solution of amylophosphoric acid is prepared electrodialytically all free electrolytes are removed, so that complications on account of the Donnan[39] effect are avoided. The cations exchange hydrogen. By use of such a material one can, on completion of the osmosis, determine electrometrically the activity of the hydrogen ions and calculate the osmotic pressure. Some results are reproduced in Table IV. I employed a solution of amylophosphoric acid, which was separated electrodialytically from potato starch solution after boiling half an hour at a temperature of 120° C. The contents of the osmometer were mechanically stirred.[40]

TABLE IV.

| Concentration in the Osmometer Per Cent. | Activity of H-ions in the Osmometer. | Observed Pressure (in mm. water). | Pressure (Corresponding) to the H-ions (in mm. water). |
|---|---|---|---|
| 2·3 | $3·6 . 10^{-4}n$ | 58·5 | 83 |
| 1·7 | $2·6 . 10^{-4}n$ | 36·5 | 60 |
| 1·0 | $1·5 . 10^{-4}$ | 16·0 | 34·7 |

It is evident that the electrometrically active hydrogen ions under conditions of free osmosis would at all times lead to a higher pressure than the solution under investigation really possesses (Hammarsten-Effect).[41, 42] There is no addition of the influences of the two ions.

As to (2), the complicated relation between pressure and concentration can be tested by calculation. Some results of pressure with variation of the concentration are given in Table V. (Compare with Fig. 2.)

TABLE V.

| Concentration in per cent. | 0·2 | 0·378 | 0·583 | 0·773 | 0·966 | 1·44 — 1·906 | 2·355 — 1·815 |
|---|---|---|---|---|---|---|---|
| Pressure in mm. water | 2·6 | 5·4 | 8·6 | 13·0 | 17·6 | 34·5    50·8 | 66·6    82·0 |

The first part of the pressure-concentration curve can be taken as practically linear ; the whole course of the curve is better interpreted by the solvation equation of Wo. Ostwald[43, 44] in the form

$$P_t = 6·21c + 14·11c^{\frac{3}{2}}.$$

[39] F. G. Donnan and A. B. Harris, *J. Chem. Soc.*, **99**, 1554, 1911.
[40] M. Samec, *Kolloid. Z.*, **59**, 266, 1932.
[41] H. Hammarsten, *Biochem. Z.*, **144**, 338, 1924.      [42] *Ibid.*, **147**, 481, 1925.
[43] Wo. Ostwald and K. Mündler, *Kolloid. Z.*, **24**, 7, 1919.
[44] Wo. Ostwald, *Kolloid. Z.*, **49**, 60, 1929.

In this equation the largest concentration deviations used (which exceed experimental error) are indicated ; one must employ a three-term equation.[40]

From such experiments one can calculate the minimal value of the " molecular weight " of the amylophosphoric acid. If we assume that the H ions have no influence on the osmotic pressure, we obtain at zero concentration the value $M = 200,000$. With a phosphoric acid content of $0 \cdot 175$ per cent. $P_2O_5$, 41667 g. of organic substances, or $258(C_6H_{10}O_5)$ groups correspond to one gram atom phosphorus. The osmotically active micelles would have then the constitution of $(C_6H_{10}O_5)_{1240} \cdot (H_2PO_3)_5$.
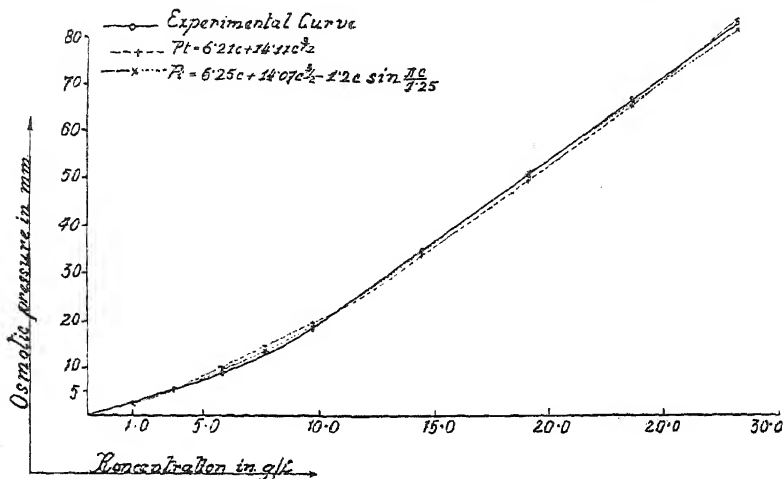


FIG. 2.

## (b) Diffusion.

The particle size of amylophosphoric acid was also investigated by diffusion.[40] This method, however, proved quite useless. The coefficient of diffusion is so great that the molecular weight would be between $M = 10,000$ and $20,000$, quite contrary to experience. Possibly the hydrogen ions or the enormous solvation tendency are the cause of these anomalies.

### Action of Alkalies and Salts upon Amylophosphoric Acid.

It is well known that starch can bind alkalies, when it is purified with dilute acids.[45, 46, 47] A small quantity of alkali is thereby completely neutralised, whilst with excess of alkali an equilibrium results between the added and combined quantity of alkali.

For more exact measurement one may satisfactorily employ the phosphoric fraction which is electro-dialytically separated from starch solution. It is prepared as a nearly transparent thick slime with a dry content of about 7 per cent. When diluted with warm distilled water to 1 per cent. dry contents the solution becomes so mobile that it can be put in an electrode cell. Potentiometric measurements with hydrogenic

[45] E. Demoussy, *Comptes rendus*, 142, 933, 1906.
[46] H. Lloyd, *J. Amer. Chem. Soc.*, 33, 1213, 1911.
[47] A. Rakowsky, *Kolloid Z.*, 11, 52, 1912.

electrodes lead to reproducible values, from which the normality of the
H ions is calculated to be

$$c_H = 15 \cdot 1 \times 10^{-5}n.$$

For every gram atom phosphorus there are about 0·6 gram ions of electro-
metrically active H ions,[30] and the 1 per cent. solution used contains
$P = 25 \times 10^{-5}$ gram atoms of phosphorus per litre. On addition of
alkalies the amylophosphoric acid can be neutralised. On potentio-
metric titration one finds characteristic relations between the added
quantity of alkali and the $p_H$ of the solution. (Compare Fig. 3.)

So long as the solution contains free amylophosphoric acid in addition
to amylophos-
phate, the $p_H$
increases only
slowly. As
soon as the
relation

1 NaOH : 1 P

is reached the
$p_H$ value in-
creases to 6·5
and remains
unchanged un-
til the relation
NaOH : P=1·6
is reached. At
this point the
solution is al-
kaline and the
$p_H$ increases
constantly with
increase of
NaOH. In
the neutral-
isation curve
amylophos-
phoric acid be-
haves analog-
ously with or-
thophosphoric
acid. An alkali
atom replaces
the first H
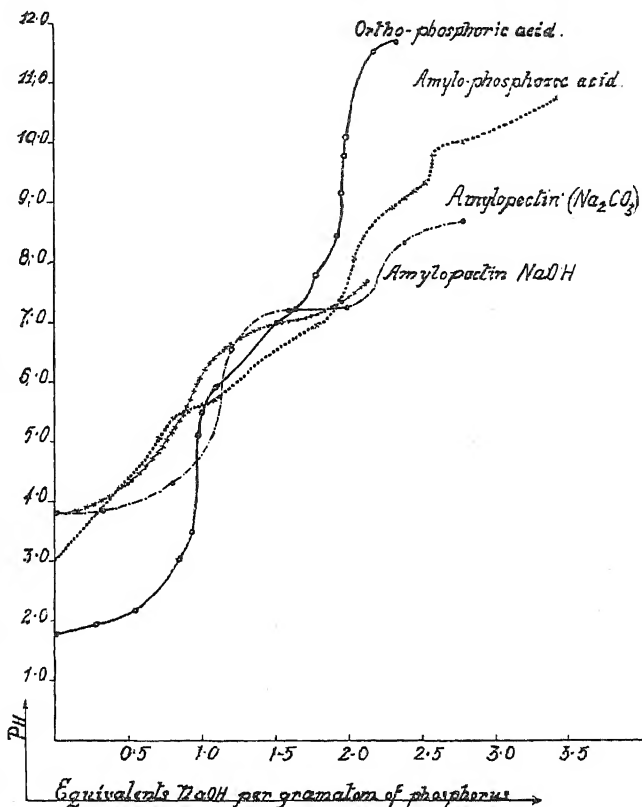


FIG. 3.

atom at $p_H = 3 \cdot 5$ and the second at $p_H = 5 \cdot 5$.

In Fig. 3 we find further the neutralisation curve of an amylophos-
phoric acid of low molecular weight, which is prepared by the action of
cold hydrochloric acid on phosphorylated starch[48] In the case of this
acid the exchange of the first H atom takes place at $p_H \cong 5 \cdot 5$, the neut-
ralisation of the second H atom is not sharp, but at all events it is com-
pleted[49] at $p_H \cong 8$.

[48] M. Samec, *Kolloidchem. Beih.*, **33**, 449, 1932.
[49] M. Samec, *Chemicky listi*, **26**, 1, 1931.

During the neutralisation the affinity to water and the viscosity of the solution change in a typical way (Table VI.).

TABLE VI.

100 g. amylophosphoric acid contain 0·175 g. $P_2O_5 = 0·0025$ gram atoms P.  Final concentration of the solution = 0·5 per cent.  One litre of this solution contains $1·25 \times 10^{-4}$ gram atoms P.

| Final concentration of the alkali. Equivalents $\times 10^4$/litre alkali . | 0·00 | 0·6 | 1·2 | 1·44 | 1·68 | 1·92 | 2·16 | 2·40 | 2·64 |
|---|---|---|---|---|---|---|---|---|---|
| NaOH : P . . . . . | 0·00 | 0·48 | 0·96 | 1·16 | 1·32 | 1·55 | 1·73 | 1·93 | 2·12 |
| $p_H$ . . . . . . | 3·823 | 4·334 | 6·033 | 6·523 | 6·571 | 7·046 | 7·117 | 7·339 | 7·687 |
| $t/t_1$ . . . . . | 3·21 | 4·01 | 2·76 | 3·33 | 3·59 | 2·39 | 3·75 | 4·04 | 4·00 |
| Precipitation by alcohol: 2 c.c. solution + 0·2 c.c. of 96 per cent. alcohol . . . . | cloudy | decreasing cloudiness | | | | | | | nearly clear |

During the neutralisation of the first H atom the viscosity increases slightly at first, then decreases and reaches a minimum at a concentration of one equivalent of alkali corresponding to one gram equivalent of phosphorus.  After this the viscosity increases with increasing value of $p_H$ (Fig. 4).
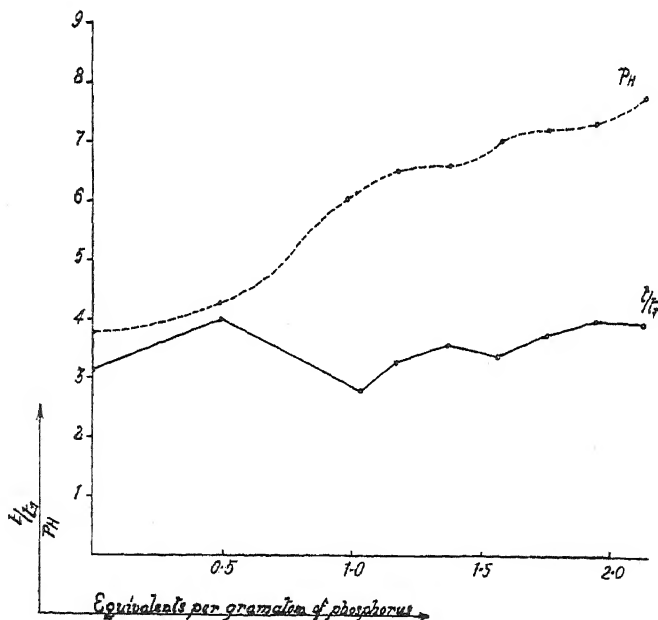


FIG. 4.

Moreover, at the second increase of the $p_H$ we see a discontinuity of the viscosity curve.

The reason of this variation of viscosity may be the following :—
The solution of amylophosphoric acid presents a structural system, wherein extremely swollen jelly-like particles are distributed in water. On addition of alkali the hydration of the amylophosphoric acid increases.  At first the jelly-like particles increase in size, whereby the viscosity increases.  The apparently jelly-like solution forms a colloidal

solution when the first hydrogen atom is neutralised, and so the viscosity decreases. On further neutralisation the hydration increases considerably with an increase in the viscosity of the solution.

Amylophosphoric acid is also precipitated from its aqueous solution by addition of alcohol. If one employs a small quantity of alcohol, one sees that on neutralisation the precipitation with alcohol decreases ; the minimum is reached at two equivalents NaOH per gram atom P and then the precipitation increases again.

Amylophosphoric acid can also be neutralised with carbonates amino-acids or albumens. By use of $Na_2CO_3$ titration curves similar to those with NaOH are obtained, but the $p_H$ jumps are still stronger. This fact can be easily explained by reason of the fact that at higher concentrations NaOH reacts also with the hydroxyl groups of the polysaccharide, whereas the carbonate acts only upon the acid groups.[30, 49] Albumens, for instance gelatin or egg-albumen, neutralise amylophosphoric acid only when they are applied in considerable stoichiometrical excess. The final $p_H$ is that of the albumen.

The amylophosphoric acid which is present in potato starch can react however also without destruction of the starch grains. If the starch grains are washed with dilute acids, the cations are exchanged by hydrogen. Such starch gives compounds with different alkalies or salts, in which the phosphoric acid and the cations are in definite stoichiometrical relation.[50] Starch seems to be neutral, if 1 gram atom phosphorus corresponds to 1·67 equivalents of cations ; we find also the same relation as at the potentiometrical titration. The properties of the potato starch, for example, the taste, the tendency to sedimentation, etc., depend of the nature of cations.

## Electrophoresis.

I have already mentioned that under influence of the electric current starch migrates to the anode. It is of interest that electrophoresis disappears if the solution becomes distinctly acid or alkaline.[2] For a 2 per cent. starch solution a final concentration of $5 \times 10^{-4}$ alkali is used. This discharge takes place at a concentration of alkali where approximately 1 equivalent alkali corresponds to one gram atom phosphorus and at which we tested the minimum of viscosity. I have already explained that it is amylophosphoric acid which is principally concerned in the electrophoresis.

Two methods have recently been used for the determination of migration velocity. H. R. Kruyt,[51, 52] by applying the Tyndall-effect observed the migration of the limit layer between the colloid solution and the overlying phase. I used the analytical method of L. Engel and Wo. Pauli[53] based upon Hittorf migration. By use of electrodialytically separated and highly purified amylophosphoric acid the Hittorf method yielded a migration velocity.

$$V = 6\cdot1 \times 10^{-5} \text{ cm./sec. per Volt/cm.}$$

H. R. Kruyt and H. J. C. Tendeloo used sols of soluble starch in the presence of salts. These were not homogeneous in their phosphorus

[50] H. Tryller, *Chem. Z.*, **44**, 833, 1910.
[51] H. R. Kruyt, *Kolloid. Z.*, **37**, 358, 1920.
[52] H. R. Kruyt and H. J. C. Tendeloo, *Kolloidchem. Beih.*, **29**, 413, 1929.
[53] L. Engel and Wo. Pauli, *Z. physikal. Chem.*, **126**, 247, 1927.

content and so it is to be expected that the migration velocity will have a smaller value, although the particles of the soluble starch are smaller than those of the amylophosphoric acid we employed. These authors found in the presence of 0·5 milliequivalents KCl,

$$V = 3·7 \times 10^{-5} \text{ cm./sec. per Volt/cm.}$$

Both results agree very well in the range of size.

## Electrical Conductivity.

Theoretically the electrical conductivity of the solutions of amylophosphoric acid is caused by the amylophosphate ions and the hydrogen ions. In solutions containing at the most 1 per cent. dry substance we find a partially linear dependence between concentration and specific conductivity (Fig. 5).

At higher concentrations the curve bends towards the abscissæ axis. The relation between electrical conductivity and the potentiometric
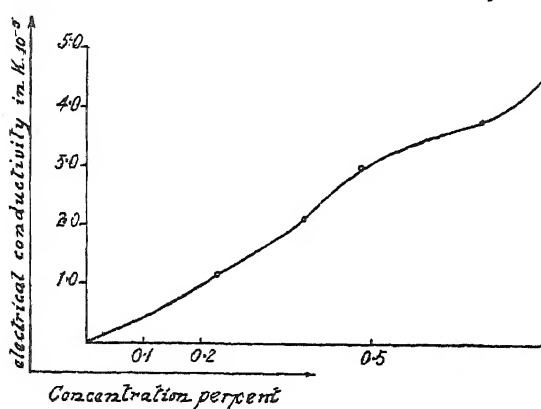


FIG. 5.

results is curious. The specific conductivity caused by H ions obtained by calculation from the electrometrically determined activity of the hydrogen ions has higher values than are experimentally observed. This phenomenon exists also with other colloids. Wo. Pauli and E. Ripper [54] found this to be the case with gum arabic sol. The large colloid ions seem to affect the hydrogen ions in their conductivity in the same way as in their osmotic behaviour.

## Phosphoric Acid in the Starch of Different Plants.

The material for all the so far described researches was potato starch. Many other species of starch were investigated in the same manner. The quality of undialysable phosphoric acid varies considerably in different starches. With the exception of *Cannabis indica* and *Curcuma domestica* ($P_2O_5 = 0·282$) potato starch contains most phosphorus. The starch of legumes, *e.g.*, the bean, the lentil, buck wheat and the pea ($P_2O_5 = 0·011 - 0·006$ per cent.) is particularly poor in phosphorus. Although they contain varying amounts of phosphorus, most starches behave like potato starch : we find in their solutions a distinct similarity in phosphorus content, H ion activity and electric conductivity (Fig. 6), so that we can employ the chemical and electrochemical laws of potato starch for other starches.[30, 35, 55]

[54] Wo. Pauli and E. Ripper, *Kolloid. Z.*, **62**, 162, 1933.
[55] M. Samec and R. Klemen, *Kolloidchem. Beih.*, **33**, 254, 1931.

Starches of the Graminees provide however an exception. They are relatively rich in phosphorus, but even after most careful purification their H ion activity and conductivity do not correspond with that to be expected fro mtheir phosphorus content (Fig. 6). This particularly is due to the

Curcuma dom.
Canna ind.
Solanum
Curcuma vir.
Amorphophallus c.
Raphanum h.
Musa par.
Colocasia esc.
Maranta ar.
Metroxylon sp.
Arenga piun.
Aeshullus hippokastan.
Arum mac.
Batatas edul.
Manichot ut.
Kastanea vesca.
Kolchicum auctumnale
Colocasia ant.
Ipamoea Jal.
Vicia fava
Lathyrus sativu
Polygonum fagopyrum
Vicia

K
CH
P₂O₅

presence of nitrogeneous ingredients which inactivate the phosphorus of the starch electrochemically and in some measure chemically also.[56] It is possible by special methods to remove a great part of the nitrogeneous substance of wheat starch, without materially decreasing the P. Wheat starch so prepared behaves electrochemically in the same manner as potato starch of similar P content.[56, 57]

## Other Atom - Groups in the Starch Affecting the Electro - chemical Change.

There are some starches whose highly purified solutions are more acid than is to be expected from their phosphorus content, e.g., certain species of Curcuma, Musa, Colchicum and also some corn starches of commerce. The reasons of these derivations are not clear in all cases. In some of these starches we find undialysable sulphuric acid. This acid is undoubtedly the cause in some corn starches of their acid properties, but it is not present in the natural starch and is introduced during the manufacture (action of $H_2SO_3$ in purification or bleaching). Starch can be readily sulphonated with $SO_2Cl_2$, whereby the acid properties are increased in the same way as by phosphorylation.[58] Moreover with many technical derivatives of starch (e.g., some soluble starches),[59] swelled starches[60, 61] and roast-dextrines,[62] the acid content of the starch cannot be entirely accounted to phosphoric acid. More exact researches on these anomalies showed that in the preparation of such starch derivatives oxidation processes took place so that carboxyl groups were formed in the molecule of the polysaccharid. As these increase the electric charge of the

Triticum
Zea mays
Marantha ar.
Oryza glut.
K
P₂O₅

FIG. 6.

[56] M. Samec, Biochem. Z., 186, 337, 1927.
[57] M. Samec, Kolloidchem. Beih., 33, 95, 1931.
[58] M. Samec, Monat. Chem., 53, 54, 852, 1929.
[59] M. Samec, Kolloidchem. Beih., 28, 155, 1929.
[60] M. Samec and M. Blinc, Kolloidchem. Beih., 38, 48, 1933.
[61] Ibid., 38, 40, 1933.
[62] M. Samec and M. Förster, Kolloidchem. Beih., 39, 464, 1934.

phosphoric acid groups and the ionic hydration they have a specific influence on the properties of the starch derivatives.

Furthermore the esterfied fatty-acids present cause an increase of the electric charge of the starch, although the esters do not contain directly ionic groups.[63]   I have several times pointed out, that a part of the dissolved substance in starch solutions is bound to the phosphoric acid and the other part is practically free of phosphorus.   This gives a blue iodine coloration by electrodialysis approximately for 1 hour of a starch solution heated to 120° C., in addition to the gel phase which contains the phosphorus (amylo-amyloses).   Another part, giving a violet-red to red iodine colour can be isolated after alternative heating and electrodialysis of the phosphoric gel (erythro-amyloses).

Exact researches pointed out that in the apparatus of Landsteiner-Pauli these polysaccharids without phosphorus also exhibit migration. The amyloses appear to be more mobile than the erythroamyloses.[64] It is not impossible that in these cases adsorbtive water contributes to the weak but distinguishable electric charge.   I may, in this connection, mention that L. Michaelis and P. Rona observed, with some carbohydrates, a minimal ionisation as at an acid and that Svanberg determined the dissociation constant to be $K = 6 \cdot 10^{-14}$

## The Electrical Double-Layer.

The above-mentioned researches were   concerned with the question whether, and in what measure, the chemical constitution of the starch molecular aggregates can explain their electrical charge and how far the behaviour of the colloid starch ions can be understood on the basis of the classical electrochemical laws for crystalloid electrolytes.   We saw that, with natural starches, phosphoric acid is the primary cause of the electrical charge and that one can in general apply the theoretical observations on solutions of true electrolytes to starch ions also.   The large colloidal ion produces however a considerable effect on the ions of H, Na, K so that the activity coefficients, the conductivity, the osmotic process and the production of a potential difference differ more than in the case of the true electrolytes.   Nevertheless one observes that changes in form of ionisation of the $ROPO_3H_2$ group cause changes in the hydration and the stability.

Apart from special consideration of the charging atom groups the electrical and colloidal phenomena of starch however invite investigation, for instance, by consideration of the changes in the electric double-layer.   H. R. Kruyt conceived that there is no fundamental difference between lyophilic and lyophobic colloids.[66, 67]   On the one hand the lyophilic colloids become lyophobic by addition of hygroscopic substances,[68] on the other hand we find that the influence of electrolytes on the viscosity of the lyophilic colloids follows completely the law of Schulze-Hardy.[69]   From this point of view H. J. Bungenberg de Jong [70]

[63] T. C. Taylor and R. P. Walton, *J. Amer. Chem. Soc.*, **51**, 3431, 1929.

[64] M. Samec and M. Blinc. *Kolloidchem. Beih.*, **30**, 163, 1929.

[65] S. Michaelis and P. Rona, *Biochem. Z.*, **49**, 232, 1913.

[66] Wo. Ostwald, *Kolloid. Z.*, **26**, 80, 1919.

[67] H. R. Kruyt and H. g. de Jong, *Z. physik. Chem.*, **100**, 250, 1922.

[68] O. Scarpa, *Kolloid. Z.*, **15**, 8 1914.

[69] H. R. Kruyt and H. G. Bungenberg de Jong, *Kolloidchem. Beih.*, **35**, 203, 1932.

[70] H. G. Bungenberg de Jong, *Rec. trav. chim. Pays Bas*, **5**, 197, 1924.

examined the viscosity of sols of soluble starch in the presence of electrolytes, as well as the precipitation of starch alkali mixtures by acetone. The general trend of the viscosity curves is analogous to my observation on solutions of natural potato starch [22], [71], [73] (Fig. 7).

Electrolytes decrease the viscosity of starch solutions and the greater the value of the cation of the added salt the greater is the influence. Bungenberg de Jong inclined to the theory of the quasi - viscous (electro - viscous)
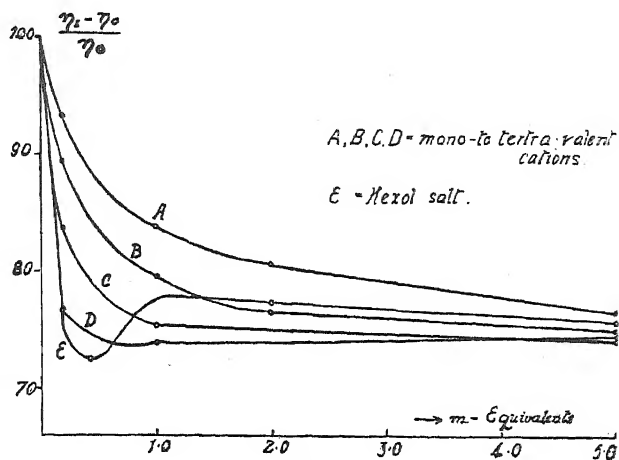


FIG. 7.

cous) effect and explained this viscosity decrease by the change of the last member in the known viscosity equation of Smoluchowsky:

$$\eta = \eta_0\left[1 + \tfrac{5}{2}\phi\left\{1 + \frac{\sigma}{\alpha^2\mu}\left(\frac{\kappa(\phi_i - \phi_a)}{2\pi}\right)^2\right\}\right],$$

which determines the influence of the electrical state of the running particle.

According to H. R. Kruyt and K. C. Winkler [74] the same equation adequately explains also the relation between the viscosity and the concentration of the starch sol. Since one can calculate, from the cataphoretic velocity of the starch sol, the potential $[\kappa(\phi_i - \phi_a)]$ this equation allows the calculation of the relative volume of the disperse phase ($\phi$) and the partical size of the starch in the starch sol.[52]

## Conclusion.

The study of starch showed in an exact manner that " impurities " present in minute quantities (which one attempts with great pains to remove in organic preparative chemistry) form a specific constituent part of the bio-colloid and brings about many of the properties of bio-colloid chemical and technical importance. Other polysaccharids have recently given similar experience. In *Isolihenin* (which much resembles starch) phosphoric acid has, in my opinion, the same rôle as in starch ; we find phosphoric acid similarly linked in the glycogen.[75] In agar-agar [76], [77] and in Caragheen [78] was found sulphuric acid and the cellulose

[71] M. Samec, *Kolloidchem. Beih.*, **4**, 132, 1912.
[72] M. Samec und S. Jenčič, *Kolloidchem. Beih.*, **7**, 137, 1915.
[73] M. Samec, *Kolloidchem. Beih.*, **8**, 33, 1915.
[74] H. R. Kruyt and K. C. Winkler, *Kolloidchem. Beih.*, **32**, 374, 1931.
[75] M. Samec und V. Isajevič, *Comptes rendus*, **176**, 1419, 1923.
[76] C. Neuberg and H. Ohle, *Biochem. Z.*, **125**, 311, 1921.
[77] M. Samec und V. Isajevič, *Comptes endus*, **173**, 1474, 1921.
[78] P. Haas, *Biochem. J.*, **15**, 469, 1921.

proved to be an oxycarbonic acid.[79] We can therefore consider the problem of a bio-colloid to be solved only when we know all those factors which regulate the surface effects of the colloid particles, in addition to its purely organic chemical constitution.

## Summary.

1. Starch owes its electric charge principally to phosphoric acid. In some starches also fatty acids and carboxyl groups contribute to the charge.

2. The phosphoric acid is present as an ester of the polysaccharid. The same is valid for the fatty acids.

3. The determination of the size of the colloid starch-ion by osmosis is difficult ; the probable value is $M = 200,000$. By osmosis we find a distinct Hammersten-effect. Diffusion yields no useful results.

4. Amylophosphoric acid reacts in solution and in the starch grain as a dibasic acid and yields salts with alkalies and other bases.

5. The migration velocity of the starch ion is $6 \cdot 1 \times 10^{-5}$ cm./sec. per volt/cm.

6. The conductivity of amylophosphoric acid is much smaller than corresponds with the electrometrically active H-ions.

7. In some starch species the phosphoric acid is masked by nitrogenous substances.

8. The viscosity changes can be explained on the basis of displacements of the ionisation, as well as by the theory of the electro-viscous effect of Smoluchowsky.

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## GENERAL DISCUSSION.

**Mr. H. B. Oakley** (*London*) said : While fully appreciating the great interest of Dr. Samec's extensive investigations on starch, may I be allowed to make a criticism of the value of the molecular weight given by him as 200,000.

While Dr. Samec gives experimental evidence (Table IV.) that purified starch has a noticeable hydrogen ion activity, yet in his interpretation of his osmotic pressure results he specifically states that he has assumed the hydrogen ions have no influence on the osmotic-pressure. It is true that calculation of this osmotic pressure from activity measurements gives much too high results, but this is no reason for neglecting the effect altogether.

The ordinary way of eliminating this " gegen-ion " activity is to make osmotic measurements in the presence of an excess of electrolyte; neglect of this precaution may lead to very much too high values of the osmotic pressure and, in consequence, much too low values for the molecular weight.

To take an extreme case we may consider my own results for gum arabic given in this volume. In these experiments a 1 per cent solution of acid gum gave an osmotic pressure of 365 mm. of water against pure water and only 8·8 mm. against N/50 H . Cl., that is to say, the molecular weight calculated from the first figure would only be one-fortieth of the truer value calculated from the second figure.

[79] E. Schmidt, K. Meinel, W. Tandebeuer u. W. Simson, *Cellubosechemie*, **13**, 129, 1932.

Of course I do not suggest that Dr. Samec's value has this order of error, but from preliminary measurements made on glycogen I have found that the osmotic pressure against pure water may be three or four times that obtained with $N/50$ KCl, and glycogen appears to be less of an electrolyte than starch.[1]

I may point out that the still lower values for molecular weight obtained by the diffusion method may be attributed to exactly the same cause, namely, failure to eliminate the effect of the ionic atmosphere around each starch particle.

**Professor M. Samec** (*Ljubljana*), in reply (*communicated*) : The values of the molecular weights I have given are calculated on the assumption that the hydrogenic *Gegenions* do not contribute to the osmotic pressure. This assumption is, it is true, not perfectly correct but, on the other hand, the error involved in the calculation of the molecular weight cannot be great.

It is possible, after alternate heating and electrodialysis of an amylopectin, to obtain starch sols which are free from phosphorus and contain no other charging atom groups. Many determinations of the molecular weights of such starch substances have been made by different methods. The values obtained varied from 150,000 to 260,000, that is to say, within the range, as shown by direct measurement, of amylopectin.

I hope soon to be able to report upon the results of osmotic pressure measurements in the presence of electrolytes; these determinations are now being undertaken.

[1] Samec and Isejivić, *Comptes rendus*, **176**, 1419, 1923.

# VERY FINE WOOD FIBRES AS COLLOID ELECTROLYTES.

By A. Lottermoser (*Dresden*).

(*Experimental work by* Th. Wilhelmi.)

The raw wood pulp made in wood grinding factories can be separated, by shaking sieves, into a coarser part, called " wood fibre "[1] and a finer one containing particles down to colloid dimensions, which is called " flour pulp " " fibre slime " or " cement pulp ". Since this cement pulp amounts to about 40 per cent. of the total pulp and since there has as yet been found no suitable application for it, it was of interest to investigate its colloid-chemical properties. With this aim the following electric potential and flocculation experiments have been made.

The potential measurements were carried out by the ultra-microscopic method, using the arrangement described some time ago by A. Lottermoser and W. Riedel [2] for the investigation of the potential of oxidehydrate sols by dilution, because we consider, from our experience, this method to be more exact than the method of the travelling boundary layer. H. Neurath and Wo. Pauli [3] have doubted the accuracy of over kind of

[1] *D.R.P.*, 542, 915.      [2] *Koll. Z.*, **51**, 30, 1930 ; **52**, 133, 1930.
[3] *Z. physik. Chem.*, **163**, 365, 1933.

measurement, because they apprehend disturbances by endosmosis of the water at the walls of the receptacle.   These authors arrive at this opinion, because they have observed an essential dependence of the values upon the diameter of the pipe, when using U-shaped pipes, and have explained this by a mobility of the water.   However, it is not correct to extend these scruples to the ultramicroscopic method, since provision is made for the influence of the glass surface upon the water mobility in the von Smoluchowski [4] equation.   We may therefore consider our measurements as being correct so long as v. Smoluchowski's formula remains acknowledged.   Moreover, we have always measured the potential of the wall as well (*l.c. 2.* " Glass "), so that we are certain that the feared positive potential of the wall cannot have taken place.

The sol of fibre slime, which served for our investigation was allowed to stand for three weeks before it was used, so that the coarser particles could settle down.   The cell we used for our electrophoretic experiments was 0·2803 cm. high, the distance between the electrodes was 1·18 cm. and the electric tension used was 10·17 volt/cm.   The distance to be passed was 0·060 mm., with slowly migrating particles 0·030 mm. The sol had a specific conductivity of $7·74 \times 10^{-5}$ mho.   The particles were of a rodlike form as was to be seen from the strong scintillation in the ultramicroscope, and they had a negative charge.   Hence mainly the influence of cations was modified in the potential and flocculation experiments.   The following salts were used :

$KCl$, $K_2SO_4$;   $MgCl_2$, $MgSO_4$;   $AlCl_3$, $Al_2(SO_4)_3$, $KAl(SO_4)_2$;   $ThCl_4$; $NaOH$.

The results are reproduced in Figs. 1 to 4.   Fig. 1 shows, that the negative charge of the wood particles is increased by the addition of $KCl$ and $K_2SO_4$.   The univalent potassium ion is incapable of diminishing the negative charge of the particles and the charge effect of the anion preponderates.   This is the more evident, since the bivalent anion affects this charge to a yet higher degree.

Magnesium salts behave differently however.   Although at low concentrations the negative potential seems to increase a little, at higher concentrations, the bivalence of the cation effects a vigorous discharge and even the sulphate ion cannot prevent this to any remarkable extent.

A quick discharge and change of potential is effected by the addition of aluminium salts (Fig. 2) and here $AlCl_3$ brings about the highest positive charge, and the smallest concentration is necessary for the discharge. It was not possible to apply $AlCl_3$ in higher concentrations because of disturbances caused by products of electrolysis at the electrodes.   Aluminium sulphate and alum gave quite similar reactions, except that the positive charge is not so strong, a circumstance that may be explained by the opposing effect of the sulphate ion, which is still stronger in alum, this being richer in sulphate.

The influence of a tetravalent cation is illustrated by Fig. 3 with $ThCl_4$.   The changes of potential are similar to those with $AlCl_3$;   the higher valency of $Th^{++++}$ shows itself in this only, that discharge occurs at lower concentrations, whilst the maximum positive potential is about the same as with $AlCl_3$.   Finally the influence of $NaOH$ has been tested (Fig. 4) and it was found, that caustic soda causes an extremely strong negative charge on the particles.

For the flocculating experiments the cement pulp sol was used and

[4] *Cf.* Graetz, *Handb. Elektr. Magn.*, **2**, 408, 1921.

FIG. I.
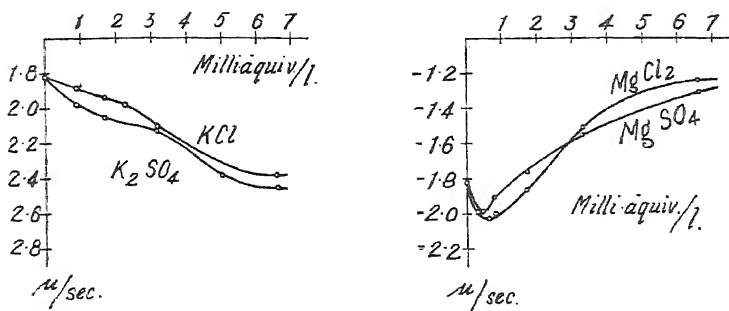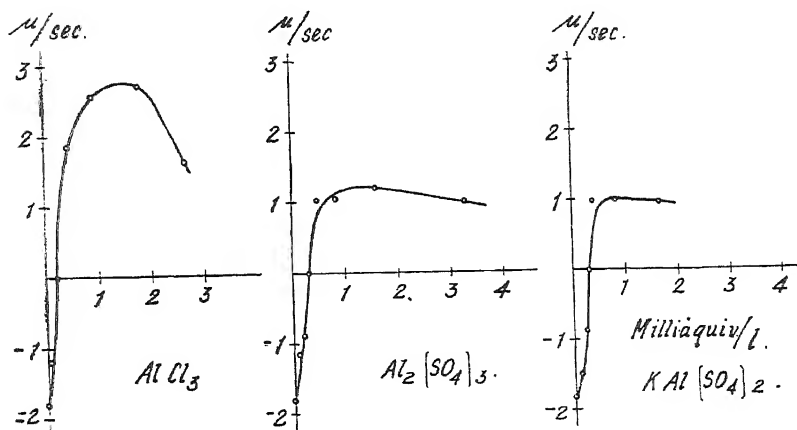


FIG. 2.
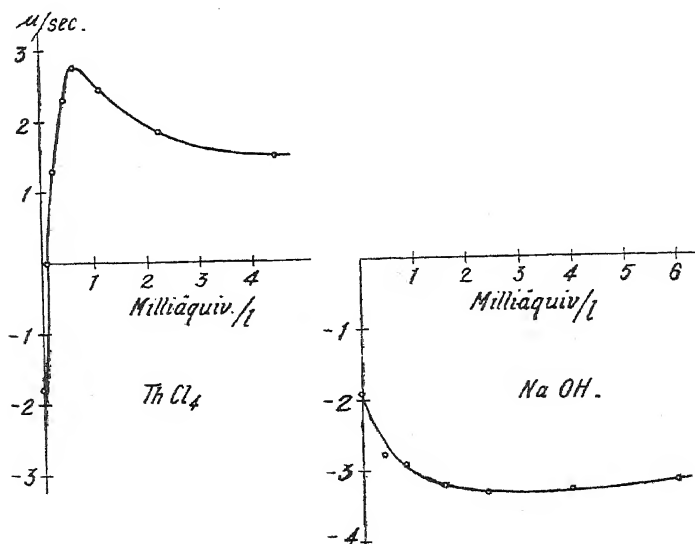


FIG. 3.                              FIG. 4.

also sols of cellulose finely ground in a Lompén mill, and of lignine, which was dispersed to a similar degree in a ball mill. The concentration was 0·1 g./l. It was so arranged that every time the necessary quantity of electrolytes has been added at once to 20 c.c. of the sol, and after shaking vigorously twice the condition of the flocculation was examined. For comparison of the effect of the various salts used the value as observed after 18 hours was taken.

At first the influence of various anions was tested by comparison of the flocculation values of the sodium salts ($NaCl$, $NaNO_3$, $Na_2SO_4$, $Na_2C_2O_4$, Na-citrate and $Na_4[Fe(CN)_6]$). All these salts flocculate to the same degree, so there is no anionic influence to be observed. This is not surprising with a negative sol and we may remember that in the potential measurements the anionic influence was also small.

By varying the cation, however, the strong influence of valency can be observed. Different cations of the same valency act in the same manner. The following table contains the flocculation values (Milli-equivalents) :

| | Cement Pulp Sol. | Cellulose Sol. | Lignine Sol. |
|---|---|---|---|
| NaCl, KCl . . | 10 | 3·4 | ∼ 25 |
| $MgCl_2$, $CaCl_2$, $BaCl_2$. | 3·4 | 2·5 | ∼ 20 |
| $AlCl_3$, $LaCl_3$ . . | 1·0 | ·2 | ∼ 4 |
| $ThCl_4$ . . . | ·03 | ·02 | ∼ ·006 |
| HCl . . . | 3·4 | 1·0 | ∼ 8 |

From this it is evident, that the cellulose sol flocculates more readily and the lignine sol less readily than the cement pulp sol and that cations of high valency flocculate very much more than univalent ones. It is also of interest to know, that the small hydrogen ion acts as strongly as the bivalent cations.

With $ThCl_4$ (but not with $AlCl_3$) in the case of all the three sols, irregular series were observed :

| | Cement Pulp Sol. | Cellulose Sol. | Lignine Sol. |
|---|---|---|---|
| 1st zone of flocculation . . | ·03 — ·1 | ·02 — ·5 | ∼ ·006 — ·01 |
| Beginning of the 2nd zone . | 1·00 | 2·5 | ∼ 20 |

We have also made experiments with more concentrated sols of cement pulp and cellulose, the results being fundamentally identical, but the flocculation values were lower. An irregular series with $ThCl_4$ was only slightly indicated.

Experiments to measure quantitatively the adsorption of the precipitating salts by the cement pulp have not been successful, because the quantities of salt absorbed are very small.

## Summary.

1. The electric potential of cement pulp, cellulose and lignine sols after addition of electrolytes has been measured. The discharging and potential varying action of the cations upon the negative sol rises with their valency ; the opposing influence of anions is only small.

2. The flocculation of these sols is exlusively determined by the valency of the cation.

3. With $ThCl_4$ the sols give irregular series.

# A NEW TYPE OF TUNGSTEN OXIDE SOL AND ITS ELECTROCHEMICAL BEHAVIOUR.

By F. Eirich (*Wien*).

## 1.

In the course of a series of experiments at the Pauli Institute, Vienna, with the object of determining the composition and properties of Bredigs metal sols,[1] tungsten-metal wires were also dispersed by an electric arc. Whereas up to the present time tungsten sols have been prepared by The Svedberg [2] exclusively by means of high frequency dispersion in organic liquids, all our sols are prepared by D.C. and in $1 \times 10^{-3} N$ sodium hydroxide. This dilute base (which proved superior to both pure conducting water and the other electrolytic solutions tested in the course of attaining uniform and stable sols) was gradually used up in the course of the dispersion. The resulting cloudy blue sol was repeatedly separated into layers, decanted and concentrated in the Pauli electro-dialyser This concentration can be carried very far, a consistent paste of 50-60 per cent. $WO_3$ being obtained without any trouble.

## 2.

The residue of the sols dried at 105° is now insoluble, immediately turns yellowish-green upon being brought to red heat, and loses 2-3 per cent. in weight. This loss of weight corresponds to a loss of water of $1 H_2O$ per 2-4 molecules of $WO_3$. The proportion $WO_3/H_2O$ increases in direct proportion to the sol concentration, whereby acid and aged sols show a steeper curve than do neutral or freshly diluted sols. Since ignition is not followed by any increase in weight, the greater part of the particles must already consist of $WO_3$, the oxidation of the blue constituent being masked by the dehydration. Probably the blue constituent consists of a somewhat lower oxide ($W_2O_5$ is an intensive blue) or of traces of metallic W.

## 3.

The sols are markedly heterodisperse, but the finest constituents are removed by the electro-decantation (E.Dec.), so that the supernatant fluid remaining after centrifuging shows only a barely discernible Tyndall-cone ; with quinoline acetate it likewise only shows a slight turbidity which arises from the precipitation of these particles ; this, however, does not indicate the presence of molecularly disperse particles. In stirring one can observe in the sol spots of different consistency occurring more frequently with the increasing age of the sols, no sparkling phenomena, however, being observed under the ultra-microscope. The Tyndall light is white.

[1] W. Pauli and F. Perlak, *Koll. Z.*, **39,** 196, 1926 ; F. Eirich and W. Pauli, *Koll. Beih.*, **30,** 113, 1930 ; W. Pauli and E. Russer, *Koll. Z.*, **58,** 22, 1932 ; F. Eirich and W. Pauli, *Koll. Z.*, **67,** 186, 1934 ; J. Löffler and W. Pauli, *Koll. Z.*, **60,** 176, 1932.
[2] The Svedberg, *Herstellung Kolloider,* Lösungen.

**4.**

During E.Dec. a concentration of the sols 10-20 fold usually takes place, and the Na-ions which initially account for practically the whole of the oppositely charged ions disappear and are replaced by H-ions. The sols which are already acid after dispersion ($p_H \simeq 5\cdot0$, depending upon the duration of dispersion) diminish their $p_H$ to about $3\cdot0$-$3\cdot3$ during the E.D. The conductivity (decreased during the dispersion from $2\cdot06 \times 10^{-4}$ ($1 \times 10^3$ $N$ NaOH) to $1\cdot3$-$1\cdot5 \times 10^{-4}$ mho.) is increased to 3-4 times this value by E.D. From this it can be seen that with this concentration a considerable reduction of the conductivity must occur. The number for a $WO_3$ molecule corresponding to an active H-ion, namely the colloidal equivalent, lies between 100 and 200, and increases with the concentration. The analytical sol-normality which can be determined by conductometric or potentiometric titration, on the other hand, increases with the concentration. In addition to this extensive concentration an increase in the particle size also results. These processes never quite cease, and are also characteristic of ageing, as is shown by a gradual decrease in the conductivity of concentrated sols on standing (in the first ten days by about 30 per cent.).

**5.**

Somewhat curious conditions are shown during the conductometric and potentiometric titrations. The initial conductivities, only approximately proportional to the sol-concentration, have already been men-



$\uparrow p H$

$P_{Na}$

$P_{Ca}$

$K_{Ca}$

$K_{Na}$

Curves of conductometric
and potentiometric
Titrations.

$\rightarrow cm^3 \begin{cases} Na \, OH \\ Ca \, [OH]_2 \end{cases}$

$\uparrow \mathcal{H}$
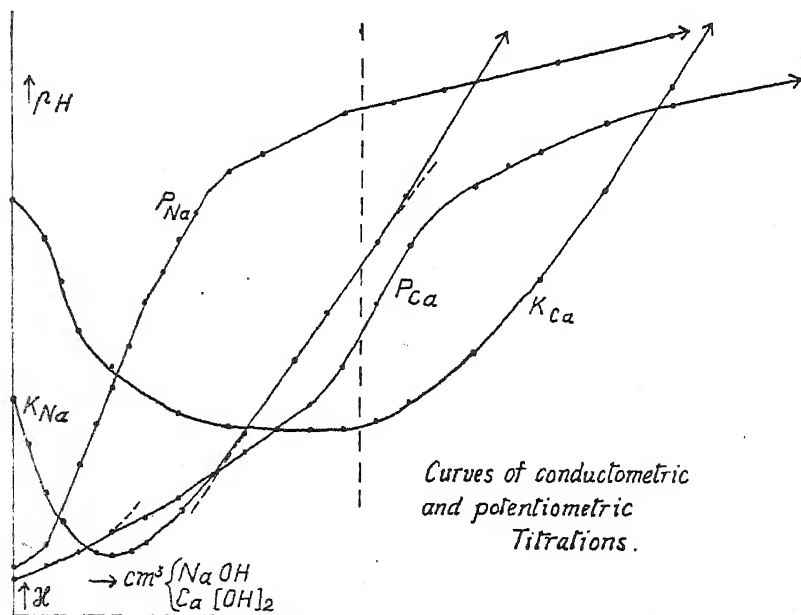
FIG. 1.

tioned. Still more striking is the fact that the lowest points of the conductometric base-titration again depends only very slightly upon the initial conductivity. The explanation of this is, however, later found in

the nature of the sols. For the alkali-titration curves fall into three separate sections (Fig. 1). The first takes the same course as the titration curve of a mixture of a strong and a weak acid, dropping sharply at first, proceeding to a well-rounded but distinct minimum, which is followed by a gradually steepening rise. This is followed by the second section, taking the form of the rising straight line of a salt with a markedly small inclination (such as would approximately be shown by a salt having an equivalent conductivity of $\Lambda \simeq 50$). These two sections approximately demand an amount of base having the proportion 2 : 1. The third section is a somewhat steeper straight line (corresponding to $\Lambda \simeq 70$) and finding practically no end. A basic straight line never occurs. The potentiometric titration-curve carried out parallel to this also falls into three sections requiring the same amounts of base as the corresponding sections of the conductometric curve. The first section shows the rapid disappearance of the active H-ions, while, close to it, the second, flattening section, instead of making the $p_H$-jump, indicates a buffer-action occurring during the neutralisation of a weak acid. The curve ends with a third, almost horizontal branch in the region of $p_H$ 6·5. If the $p_H$ is increased above this by the addition of a large amount of base, it returns to the old value in the course of a few minutes, indicating a slowly progressing complete reaction.

## 6.

An elaboration of these results was obtained by us by means of titrations with calcium hydroxide. The conductometric curves here separate into a falling, reversed S-shaped, branch and developing into a very flat minimum, into a second, slowly rising branch which likewise never reaches the basic straight line and finally becomes a straight line of the same inclination as that seen in the case of the basic alkali-titration, corresponding to $(\Lambda \simeq 70)$. The falling and the flat branch up to the re-clevation requires the same amounts of base as the two first branches of the alkali-titration and obtains its curious shape by reason of the adsorption of Ca-ions and the flocculation of the sol which follows. The first Ca-ions adsorbed may represent strong positive centres on the surface of the particle, which is densely occupied by associated H-ions and therefore electrostatically facilitates their dissociation.* The continued adsorption results in coagulation ; both the ions present in the sol initially, as well as the added $Ca^{++}$- and $OH^-$-ions, disappear from the solution and the conductivity undergoes a considerable decrease. This is immediately followed by the formation of the undissociated Ca-salt from the likewise weak acid on the particle surface (which also is dissociated with difficulty), the conductivity meanwhile remaining unchanged, whereby the broad minimum is caused. After this a continuously rising branch recommenced (which never reached the basic straight line during our experiments) ; this probably leads to a reaction with the nucleus in which, apparently, enough soluble acid salts are either formed or are separated from the surface of the particle, to afford an increase in the conductivity. The potentiometric titration with calcium hydroxide, subsequent to an almost uniform and gradual increase of the $p_H$ up to

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* This phenomenon was also observed by Rabinovitsch [3] and designated as supra-equivalent replacement.

[3] Rabinovitsch and V. A. Kargin, *Z. physik. Ch.*, **133**, 203, 1928 ; Rabinovitsch and W. A. Dorfmann, *Z. physik. Ch.*, **131**, 313, 1928 ; Rabinovitsch and E. Laskin *Z. physik. Ch.*, **134**, 387, 1928.

the end of the flat minimum of the conductivity curve and a short steep section ($p_H$-increase approximately from 4·5-5·5) thereafter, results in a further flattening branch, which, somewhat more gradually, approaches the same final value of $p_H = 6·5$, as in the case of the alkali titration.

## 7.

We can therefore distinguish in our sols, two main constituents which react differently with a base. The first constitutes only a small but almost constant fraction of the sol, and consists of a strongly dissociating and two weak acid stages ; the second reaction, which takes time, is effected on the nucleus. Thus, the existence of a special charging constituent seems to be proved. With regard to its constitution I speak only of one combination. Copeaux (1909) sought to describe some type of tungsten oxide acids also as complex hetero-poly-tungsten acids. Consequently they can be written as a hydrated compound: $H_{10}[H_2(W_2O_7)_6]$ isomorph, with, for example, $H_9[B(W_2O_7)_6]$ and analogous to six water molecules : $6H_2O = H_{10}[H_2(O)_6]$. The behaviour of those acids and salts was found in quite good agreement with this formula, except for the fact they never were found ten-basic but at most six-basic $R_6H_4[H_2(W_2O_7)_6]$. Sometimes it seemed also better to take only the half formula : $R_3H_2[H(W_2O_7)_3]$. Such a composition of this sodium salt would explain the behaviour of our sols on neutralisation. I do not, however, desire to maintain a sharp separation of this constituent from the nucleus of the particle. It is probably nearer the truth to imagine the whole particle subjected to a swelling process, and built up, somewhat in the manner of hydrous crystals, out of $WO_3$-hydrates. The water content of these hydrates in the first layer may correspond to our tribasic acid and decreases rapidly from the surface towards the inside of the particle, thereby passing through compositions which correspond consecutively to different types of tungstic acids, and which are in equilibrium among the surface layer and the nucleus.

## 8.

In this connection another curious instance may be mentioned. If the conductivity of the sol is calculated from the amount of the potentiometrically determined H-ions with the assumption of a sufficiently low colloidal ion mobility of 10, the values obtained are twice as high, on the average, as those actually measured. The activity of the current-conducting ions therefore is considerably smaller than that of those acting on the hydrogen-electrode. A similar behaviour was already observed by Wo. Pauli [4] and his co-workers in a series of highly charged, pure,[5] positive or negative sols, and considered as a consequence of the assymmetrical distribution of ion charge in the sense of the modern theory of electrolytes. The divergence between conductivity, concentration and base titre initially mentioned may be illustrated by some individual different coefficients of deviation.

## 9.

Of the flocculations carried out, those treated with KCl are fully reversible after washing with distilled water, and those carried out with

[4] W. Pauli and E. Ripper, *Koll. Z.*, **62**, 162, 1933.
[5] W. Pauli and E. Valkò, *Koll. Z.*, **66**, 312, 1934.

$CaCl_2$ are partly reversible. After addition of $AlCl_3$ these flocculated particles still contain a certain amount of water, but they can no longer be peptised by washing. The threshold values were found to lie at $1 \times 10^{-2}$ $N$ KCl or $5 \times 10^{-4}$ $N$ $CaCl_2$ respectively. The flocculation concentration for $AlCl_3$ is dependent on the concentration and lies still lower. No change of charge could be ascertained, although we went up to very high concentrations (pouring into a 2-mol. solution). Quite similar was the behaviour exhibited by the oxychloride of zirconium. If we follow up the conductivity of one of our sols when $AlCl_3$ is added, we find that it rises markedly up to the equivalence of the Al-ion and sol-normality. Flocculation begins at once, resulting in a flattening of the curve, which, later on, during the addition of about three times the equivalent amount, gradually flattens out and merges into the straight line which depends upon the $AlCl_3$-addition alone.

## 10.

We now proceed to the recharging experiments with four different $Al_2O_3$-sols. These had been prepared according to the process of Pauli and Schmidt,[6] containing 2 per cent. to 3 per cent. aluminium oxide, were of great purity throughout, had a $p_H > 4\cdot8$ and were very highly charged. Their colloidal equivalents were 24, 37, 74, and 88. The chlorine activities were four to twenty times higher than H-ion activities of the $WO_3$-sols to be recharged. When the sols were mixed, the following facts were observed : if the tungsten-sol is in excess, the mixture remains stable until the chlorine-activity of the $Al_2O_3$-sol, recalculated for the total volume, attains approximately 20 per cent. of the H-activity of the $WO_3$-sol. In the case of larger additions (up to those somewhat in excess of the equivalence), flocculation of the whole mixture occurs. Starting from twice the equivalent amount of $Al_2O_3$-sol, the mixture again remains stable and takes a cathodic path. The charge of the $WO_3$-sol has therefore been reversed. If more than five to six times the amount necessary for a reversal of charge is added, a small proportion of the $Al_2O_3$-sol, curiously enough, precipitates out, while the rest remains bluish and stable. The same also occurs when small amounts of $WO_3$-sol are poured into the $Al_2O_3$-sols. The phenomenon is, however, only true in the case when the two most highly charged $Al_2O_3$-sols are used. The third sol $(K = 74)$ effects only an uncomplete reversal. The fourth $(K = 88)$ flocculates at all quantitative proportions and the flocculate is blue. The role which is played by the colloidal equivalent (*e.g.*, density of charge), and chlorine-activity (*e.g.*, sol-normality) here, is recognised when the $WO_3$-sol is treated with one of the two most highly charged, but half-diluted $Al_2O_3$-sols. The reversal of charge then occurs when double the amount of sol is added, but, in the case of the sols bearing a weaker charge no reversal of charge occurs, even if the chlorine-ion activity then reaches the same height as in the case of the charge-reversing amounts of the other sols. The reversal of charge depends consequently on both the amount and the density of charge of the particles of opposite sign ; so that a reversal of charge will never occur below a certain density of charge in any quantitative proportion whatever.

[6] Pauli and E. Schmidt, *Z. physik. Ch.*, **129**, 199, 1927.

### 11.

We also observed the process of charge-reversal conductometrically, both by measurements in the freshly mixed sols and by a true titration of a $WO_3$-sol sample with the $Al_2O_3$-sol. Hereby we obtained the results shown in Fig. 2. During the first addition the conductivity in the still stable mixture remains approximately constant, or falls to a small minimum. After this there is a rapid linear rise, accompanied simultaneously by flocculation. When the equivalence of both sols is reached, a break occurs. The rise now continues, also linear but flatter, while the reversal of the charge grows increasingly complete. When the chlorine-ion activity lent to the mixture by the addition of the highly charged $Al_2O_3$-sols has reached four to five times the equivalence, a new break occurs in the curve and the conductivity now rises in strict proportion to the amount of sol added. The latter happens with the non-reversing sols just after the simple equivalence is reached. These straight end sections lie exactly parallel above the sol-dilution lines, the values for the single mixtures being five times higher than those for the titration (continuous additions). In our case this difference amounts to $5 \times 10^{-4}$ mhos. in the first and $1 \times 10^{-4}$ mhos. in the second case. The conductivity for the point of equivalence, also, is higher by $5 \times 10^{-4}$ mhos. than that of the unchanged $Al_2O_3$-sol at the same dilution. This increase corresponds to $1 \cdot 5 \times 10^{-3} N$ hydrochloric acid liberated by the flocculation, provided that the disappearance
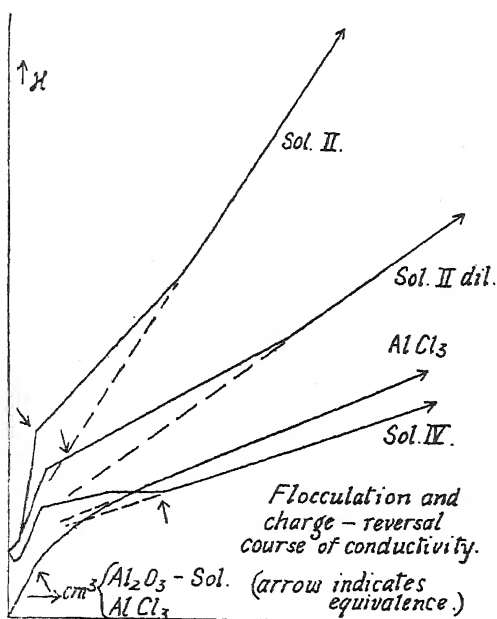


FIG. 2.

of the conducting positive sol-particles is taken into account. Exactly $1 \cdot 5 \times 10^{-3} N$ H-ions are also liberated in this sol by flocculation with $AlCl_3$ and titrated with sodium hydroxide until the lowest point of the conductometric curve is reached. The charge of the $Al^{+++}$- or colloidal ions adsorbed by the flocculation is thus equivalent to the normality of the strong groups in the sol. An increased adsorption is apparently prevented by the disappearance of the free particle-charge and the increasing competition of the H-ions. If these are continuously neutralised, and new places for occupation are thus made available, further constituents can actually be brought into the reaction, such as was also the case in our titrations with calcium hydroxide.

If we summarise those last paragraphs, which deal with flocculation and reversal, they show that the different valences or varied colloidal

equivalences of the added ions or sols with positive charges are followed by characteristic changes of the stability of our negative sols. Decrease of the free charge, mutual flocculation of colloids and reversal may consequently be called forth by such alterations of conditions, that they appear as related processes in respect to their mechanisms.

## Summary.

1. The new type of tungsten oxide is a very typical colloidal electrolyte with well reproducible qualities.
2. A strong charge caused through the dissociation of a small amount of tungsten acid is responsible for their stability.
3. The $WO_3$ molecules building up in the main the particles are adapted to become hydrated and then to react with bases.
4. In the sols one notices a material decrease of the conductivity coefficient.
5. One can observe a substantial flocculation with ions of surplus positive valences or positive colloids. The reversal is only successful with $Al_2O_3$-sols of very small colloidal equivalent, its course can be studied very well by conductivity measurements. An amount of acid is released, which is equivalent to the normality of the strong dissociating part of the sol.
6. A relationship between the flocculation, mutual colloid reaction and reversal is mentioned.

## AUTHOR INDEX.

# ADDENDA.

Page 61 : In middle of long paragraph : For *Gegenionen* read *Nebenionen*.

Page 152, at end of paper, add : Subsequent experience with sulphonic acid derivatives of the paraffins studied in dilute solutions has shown that these are very similar to the soaps but definitely weaker. The graphs for the soaps in Figs. 1 and 2 should not have been made to conform to that for a fully dissociated electrolyte even in extreme dilution. Hence, the activities for the higher soaps in Table I. will all be slightly smaller than there indicated.

Page 157, to the heading of the 4th column of Table II., entitled " NaCl coul." add footnote :

‡ Corrected for sodium chloride carried in sorbed condition on curd fibres as discussed below in section "Sorption of Chloride by Curd Fibres."

Page 257, before Mr. Robinson's contribution, add :
**Mrs. Laing McBain** (*Stanford, Cal.*), said : With the porous disc method diffusion results can be distorted, through the effects of sorption, if the precaution is not taken first to establish the diffusion columns and only then to begin the actual experiment, after replacing with fresh liquid on both sides of the disc as was emphasised by McBain and Liu. One would also like to inquire whether streaming was tested for by Dawson's method with G3 membranes, and whether the cell constants were the same before and after the experiments with the dye in Dr. Hartley's experiments.

Page 336, footnote 5, for *ssq.* read 559.
Page 340, 5th line, read $SO_4^=$.
Page 343, top line, read *were* for *we*; footnote 14, read *Hermann*.

Page 355, before Prof. Gorter's contribution add :
**Dr. A. Neuberger** (*London*) said : All the evidence available seems to show that the combination of proteins with hydrogen or hydroxyl ions is a chemical phenomenon, and not due to adsorption. It seems that the free groups of the trivalent amino acids, the free carboxyl groups of the di-carboxylic amino acids, the basic groups of lignine, arginine and histidine, and the phenolic group of tyrosine are mainly responsible for the acid and base binding of proteins. The peptide linkage does not come into play. It can be shown that the titration curve of proteins is explained by the derivation constants of the constituent amino acids.

# ABSORPTION SPECTRA OF SOME COMPLEX SALTS IN DIFFERENT SOLVENTS.

## (Contributions to the theory of Co-Ordinate linkage VI.)

### By R. Samuel and Mumtaz Uddin.

This paper forms part of a series of investigations [1] on the optical behaviour of complex salts. Recently Samuel and Nazir Ahmad (III., Part 2) studied the influence of the field produced by foreign ions on the absorption spectra of complex salts and this investigation has now been extended to complex ammines.

The absorption spectra of the following salts have been investigated : $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_5NO_2]SO_4$, $Na_2[Fe(CN)_5NO]$, $Na_3[RhCl_6]$, $K_2[PtCl_4]$.

The behaviour of each of the above salts was examined in saturated solutions of inorganic salts of the type of sodium chloride, potassium chloride, potassium bromide, etc.

The absorption spectrum is described by the absorption coefficient $K$/wave-length curve. The absorption coefficient is here defined by the expression $I = I_0 \ 10^{-Kcd}$, where $I_0$ is the original intensity of light, I the intensity of light after absorption, $d$ and $c$ stand for thickness and concentration of the solution. The experimental method was the same as described in earlier papers of this series.

## Experimental Results.

### 1. Hexammino Cobaltic Chloride [Co(NH₃)₆]Cl₃.

The absorption spectrum of this salt was investigated in concentrated solutions of sodium chloride, potassium chloride and potassium carbonate. Various maxima are represented in Fig. 1, and in the table on next page.

The first maximum at about 480 m$\mu$ is of a more diffuse character than that observed in distilled water (*cf.* I. and III.). The subsidiary maxima observed at 512 and 435 m$\mu$ are only slightly developed in the presence of foreign ions. The most important maximum in all the three cases is shifted relatively to values in water, and the values of log $K$ are slightly decreased. The interchange of Na and K ions does not appreciably alter the values of $K$ or the wave-lengths ; the interchange of negative ions, however, gives rise to different values of log $K$ and wave-lengths.

The second maximum at about 350 m$\mu$ shows a similar behaviour. The subsidiary maximum observed in water at 358 m$\mu$ is not present in the

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[1] Earlier papers of this series are : (I.) R. Samuel, *Z. Physik,* **70,** 43, 1931 ; (II.) R. Samuel and Advi Rao R. Despande, *ibid.,* 80, 395, 1933 ; (III.) R. Samuel, A. Hafiz Khan and Nazir Ahmad, *Z. physik. Chem.* **22B,** 431, 1933 ; (IV.) R. Samuel and Mohd. Jan Khan, *Z. Physik,* 84, 87, 1933 ; (V.) Must. Karim and R. Samuel, *Bull. Ac. Sc. Unit. Prov.* (Allahabad), **3,** 157, 1934. Quoted herein as I., II., III., etc.

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Table of Absorption Maxima.

| | 1st Maximum. | | 2nd Maximum. | | 3rd Maximum. | | 4th Maximum. | |
|---|---|---|---|---|---|---|---|---|
| Solvent. | Log $K$. | $\lambda$ in $m\mu$. | Log $K$. | $\lambda$ in $m\mu$. | Log $K$. | $\lambda$ in $m\mu$. | Log $K$. | $\lambda$ in $m\mu$. |

**1. Hexammino Cobaltic Chloride.**

| Solvent | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ |
|---|---|---|---|---|---|---|---|---|
| Water . . . | 1·90 | 482 | 1·60 | 349 | | | | |
| NaCl . . . | 1·70 | 486 | 1·55 | 338 | | | | |
| KCl . . . | 1·73 | 486 | 1·50 | 339 | | | | |
| $K_2CO_3$ . . . | 1·78 | 476 | (1·66) | (335) | (2·20) | (283) | (2·65) | 255 |

**2. Pentammino Cobaltic Chloride.**

| Solvent | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ |
|---|---|---|---|---|---|---|
| Water . . . | 2·4 | 525 · | 1·30 | 345 | 3·00 | 280 |
| $Na_2SO_4$ . . . | 1·78 | 506 | 1·86 | 359 | | |
| $Na_2CO_3$ . . . | 1·95 | 502 | 2·20 | 343 | (2·70) | 305 |
| $K_2CO_3$ . . . | 1·84 | 503 | 1·80 | 352 | (2·80) | 276 |

**3. Pentammino Nitro Cobaltic Sulphate.**

| Solvent | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ |
|---|---|---|---|---|
| Water . . . | 2·3 | 455 | 3·3 | 339 |
| NaCl . . . | 2·20 | 451 | 3·48 | 338 |
| KCl . . . | 2·19 | 447 | 3·39 | 338 |
| KBr . . . | 2·15 | 446 | 3·38 | 336 |

**4. Sodium Nitroprusside.**

| Solvent | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ |
|---|---|---|---|---|---|---|
| Water . . . | 1·75 | 512 | 1·60 | 400 | 3·70 | 276 |
| Sodium Chloride . | 1·02 | 485 | 1·37 | 373 | (3·44) | 256 |
| Potassium Chloride . | 1·00 | 480 | 1·37 | 383 | (3·44) | 255 |
| Potassium Bromide . | 1·00 | 486 | 1·38 | 387 | (3·54) | 258 |

**5. Sodium Rhodi-hexachloride.**

| Solvent | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ |
|---|---|---|---|---|---|---|
| Water . . . | 1·80 | 503 | 1·80 | 392 | 3·5 | 285 |
| NaCl . . . | 2·20 | 520 | 2·08 | 409 | | |
| KCl . . . | 2·20 | 516 | 2·10 | 407 | | |
| KBr . . . | 2·60 | 540 | (2·62) | 420 | | |
| $Na_2SO_4$ . . . | 2·12 | 500 | 2·11 | 398 | | |

**6. Potassium Platino-tetrachloride.**

| Solvent | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ |
|---|---|---|---|---|---|---|---|---|
| $H_2O$ . . . . | 1·29 | 469 | 1·76 | 381 | 2·08 | 318 | 2·32 | 265 |
| NaCl . . . | 1·19 | 482 | 1·89 | 393 | 1·88 | 336 | 2·66 | 254 |
| KCl . . . | 1·11 | 465 | 1·84 | 392 | 1·82 | 325 | 2·66 | 257 |
| KBr . . . | 1·28 | 508 | 2·00 | 413 | 2·65 | 308 | 3·94 | 267 |

**7. Potassium Platino-tetrachloride.**

| Solvent | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ | Log $K$ | $\lambda$ |
|---|---|---|---|---|---|---|
| NaCl . . . | 1·19 | 482 | 1·89 | 393 | 1·88 | 336 |
| KCl . . . | 1·11 | 465 | 1·84 | 392 | 1·82 | 325 |
| KBr . . . | 1·28 | 508 | 2·00 | 413 | (3·99) | (266) |

curves for different solvents. Here also the maximum shifts against the water values. The exchange of Na for K gives a small displacement, but exchange for the $CO_3$ ions produces a considerably greater change. In $K_2CO_3$ solution the maximum cannot be very accurately defined, because it is already overlapped by the continuous absorption on the short wave-length side. The introduction of $CO_3$ ions not only produces a definite shift in absorption, but also gives rise to new maxima. One of these is at 255 m$\mu$ and the character of the curve indicates the existence of another at 283 m$\mu$ in the continuous portion.
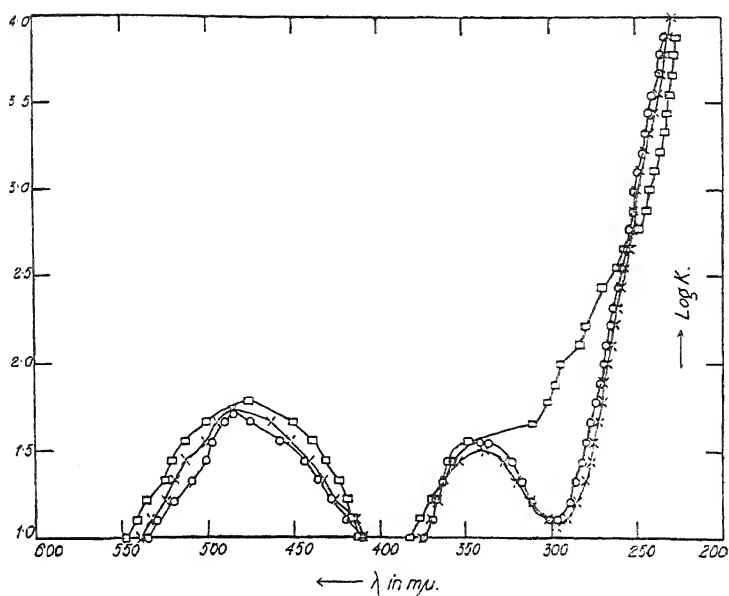
FIG. 1.—[Co(NH$_3$)$_6$]Cl$_3$ in saturated solutions of : ⊙ NaCl, × KCl, ▫ K$_2$CO$_3$.
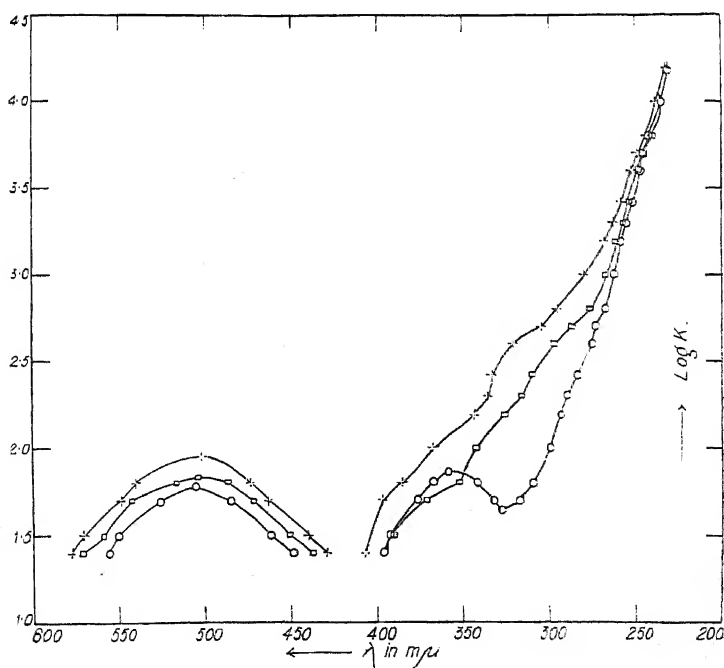


FIG. 2.—[Co(NH$_3$)$_5$Cl]Cl$_2$ in solutions of : ⊙ Na$_2$SO$_4$, + Na$_2$CO$_3$, ▫ K$_2$CO$_3$.

## 2. Pentammino Cobaltic Chloride, $[Co(NH_3)_5Cl]Cl_2$.   (Fig. 2.)

This salt has been investigated in the concentrated solutions of sodium sulphate, sodium carbonate and potassium carbonate, and the absorption maxima observed are given in the table.

The behaviour of this salt is very similar to that of the previous compound.   The values of wave-lengths of absorption maxima are almost identical with $Na_2CO_3$ and $K_2CO_3$.   In the second maximum the band head cannot be very accurately defined owing to overlapping of the curve by continuous absorption.   In the presence of $CO_3$ ions, a new band again makes its appearance at about 276 m$\mu$, similar to that observed for $CO_3''$ in the discussion of the last salt.
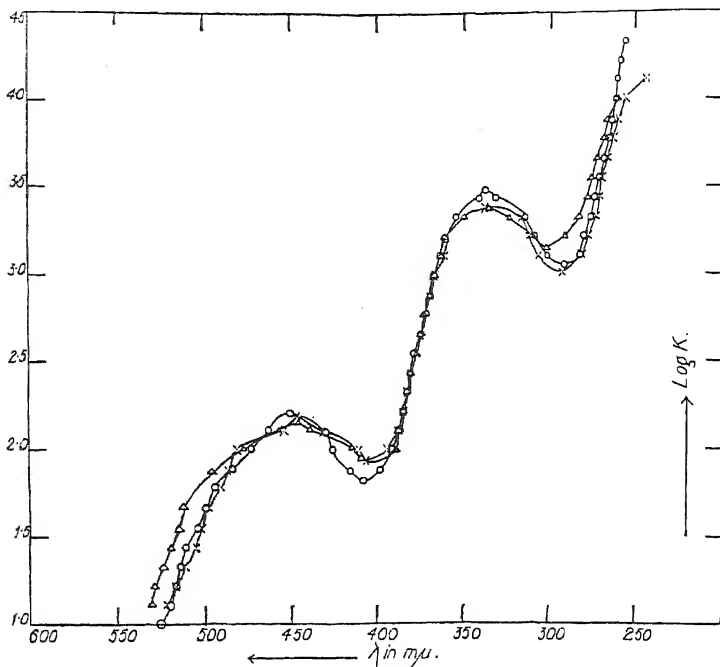


Fig. 3.—$[Co(NH_3)_5NO_2]SO_4$ in saturated solutions of: ⊙ NaCl, × KCl, △ KBr.

## 3. Pentammino Nitro Cobaltic Sulphate, $[Co(NH_3)_5NO_2]SO_4$.   (Fig. 3.)

The absorption spectrum was investigated in sodium chloride, potassium chloride and potassium bromide solutions.   The absorption maxima are given in the table.

In this case the displacements of wave-lengths of the absorption maxima are greater on exchange of potassium for sodium.   All values of log $K$, and also the values of the spectral position of the maxima, even without additional foreign ions in the solution, are widely different from those of $[Co(NH_3)(NO_2)]Cl_2$ (see I. and III.), since the maxima of this substance have been determined at 502 m$\mu$ (log $K = 1\cdot8$) and 345 (log $K = 1\cdot4$).   The log $K$ values are different in case of sodium chloride and potassium chloride solutions, but they are very nearly the same in the KCl and the KBr solutions.

In the second maximum, by exchange of sodium and potassium, different values of log $K$ are obtained, but with the exchange of bromine and chlorine the values for log $K$ and for the wave-lengths are identical.
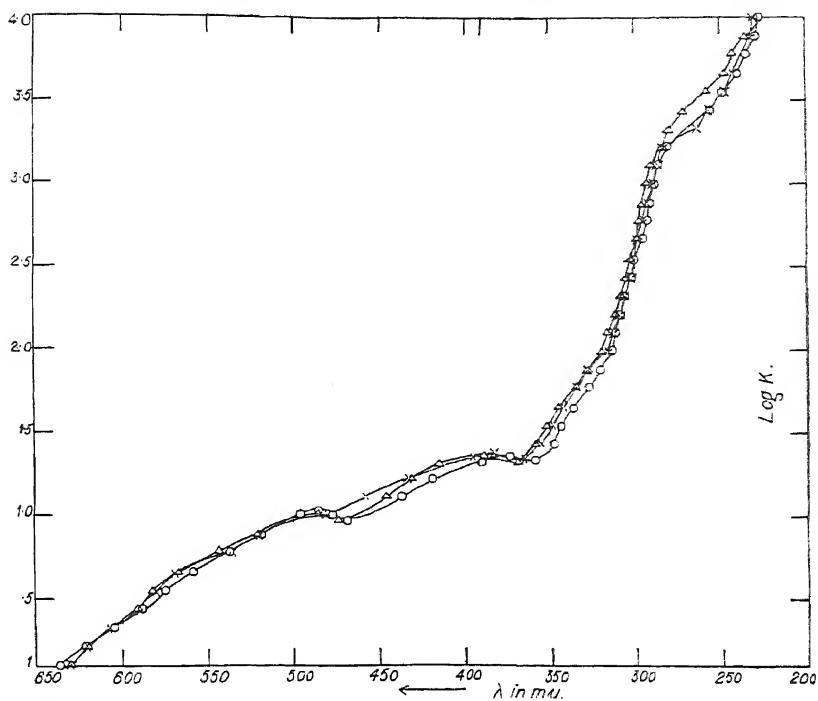
FIG. 4.—Na$_2$[Fe(CN)$_5$(NO)] + 2H$_2$O in saturated solutions of : ⊙ NaCl, × KCl, △ KBr.
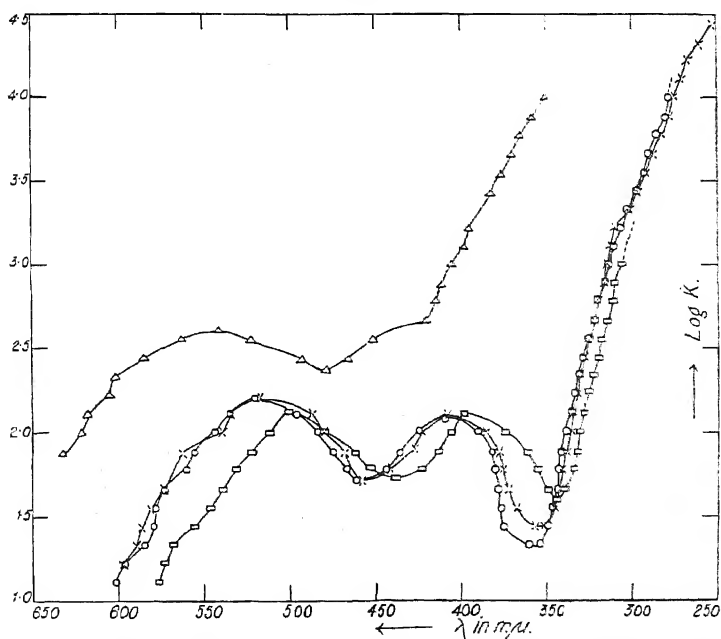


FIG. 5.—Na$_3$[RhCl$_6$] in saturated solutions of : ⊙ NaCl, × KCl, △ KBr, ⊡ Na$_2$SO$_4$.

**4. Sodium Nitroprusside, $Na_2[Fe(CN)_5NO]$.** (Fig. 4.)

The absorption curves obtained were of a very diffuse character and the absorption maxima were not well defined.    Indeed, it would be difficult to correlate the maxima without the help of the curve for the aqueous solution of the salt (see I.).    The slight maxima found in water at 448 and 345 m$\mu$ are so diffused that they cannot be measured at all.    Displacement takes place by the exchange of positive ions in the region of longer wavelengths, whereas in the region of 260 m$\mu$ and downward to short wavelengths the effect of the exchange of the negative ion is noticeable.

**5. Sodium Rhodi-hexachloride, $Na_3[RhCl_6]$.** (Fig. 5.)

There is a small displacement of the whole curve in this case when the positive ions are exchanged while the negative ions remain the same.    If, however, the negative ion is changed, there is a most striking displacement of the absorption curve.    In the case of KBr, the whole shape of the curve is altered.    The subsidary maximum measured at 285 m$\mu$ in water (*cf.* II.) therefore becomes indistinct in the presence of foreign ions.
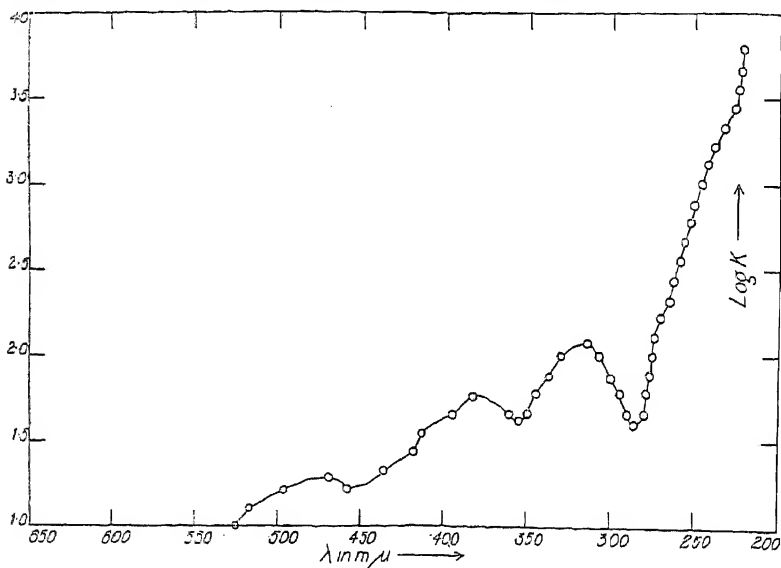


FIG. 6.—$K_2[PtCl_4]$ in distilled water.

**6. Potassium Platino-tetrachloride, $K_2[PtCl_4]$.** (Figs. 6 and 7.)

As the absorption curve of this salt had not been previously measured, we show in Fig. 6 the curve of this salt undisturbed in aqueous solution. The maxima are recorded in the following table, together with those of some other salt from earlier measurements (see II. and III.) for comparison purposes.    The main maxima are italicised ; figures in roman characters show subsidary maxima :—

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $K_2PtCl_4$ . | | | *469* | *381* | *318* | | 265 | 225 |
| $H_2PtCl_6$ . | | (486) | 455 | 375 | | 285 | 262 | |
| $K_2PdCl_6$ . | 570 | 535 | 445 | 340 | | 280 | 243 | |
| $K_2PdCl_4$ . | | | *430* | | 303 | | 240 | |

In (III.) certain empirical rules were deduced with regard to the appearance of selective absorption bands in complex molecules and $K_2[PtCl_4]$ behaves in accordance with these.    The bands are found in the ultra-violet region which appear in those salts in which ions are linked to the

central atom, and a band appears in the neighbourhood of 450 m$\mu$ which is characteristic of co-ordinated chlorine ions.

In the presence of foreign ions similar results are obtained, as in the case of $Na_3[RhCl_6]$. Here again, the absorption curve is not much affected by the exchange of positive ions, but the exchange of Cl$^-$ for Br$^-$ produces a displacement of the whole curve. The absorbing power of the band at 265 m$\mu$ is strikingly strengthened, and at this stage the curve does not follow Beer-Lamberts Law.
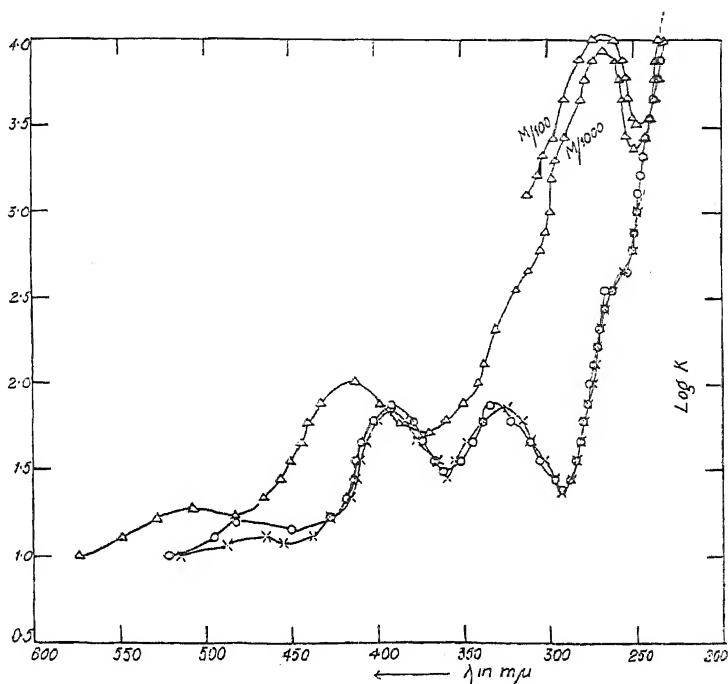


FIG. 7.—$K_2[PtCl_4]$ in saturated solutions of : $\odot$ NaCl, $\times$ KCl, $\triangle$ KBr.

## II. Conclusions.

In the absorption spectra of the cobalt ammines, two main absorption maxima at about 500 m$\mu$ and about 350 m$\mu$ are observed. In (I.) and (III.) it was shown that these absorption maxima appear in all compounds containing nitrogen linked to the cobalt ion irrespective of whether the nitrogen atom forms a part of $NH_3$, $NO_2$, ethylene diamine or NO groups. As a result of the present investigations it is seen that these absorption maxima are displaced sometimes under the influence of the positive and sometimes under that of the negative ions of the solvent. It appears that the occurrence of this displacement is due to the electrovalent character of the complex salts. Naturally, if the co-ordination complex is a positive ion itself, the negative ions of the solvent will surround it, and the complex ion (the bearer of the selective absorption) is in a negative field. If, however, the complex is a negative ion itself, then positive ions of the solvent will form a surrounding cloud such that it is in a positive field. Displacement is therefore to be expected when the complex ion is in any field positive or negative. Variations in the

field, that is the exchange of the negative ions of the solvent in the case of a complex cation or the exchange of the positive ions of the solvent in the case of a complex anion, results in the displacement of the two above-mentioned absorption maxima.

In measuring the absorption of complex ions in the presence of foreign ions two effects must always be considered :—

(i) *A molecular Stark effect* will change mainly the values of the ab-sorption coefficient ; but it will not very much affect the wave-length of the maximum in question. In solution we measure in reality the envelope of a band system which cannot be resolved. Each line will be split in the electric field into a number of components, the more so as the field is not defined ; on the contrary, the number of foreign ions sur-rounding the complex ions and their distance from them may differ widely. This splitting up of the original lines will mainly bring about a distribution of different intensity in the envelope.

(ii) *A deformation of the molecule*, especially a change of the internuclear distance, will affect the curves of potential energy of the different elec-tronic levels in a different way, so that the energetical distances between them are changed, with production of a displacement of the absorption maxima in the spectrum. These conclusions have already been drawn in (III.) from the different manner in which particular bands are influenced by the presence of foreign ions in the solution.

The character of the changes observed in the ammino-cobaltic com-plexes indicate that the molecular Stark effect is the main effect rather than a strong displacement of the maximum due to the deformation of the molecule. This is in good agreement with (III.). The diamagnetic cyanides show slight displacement of their characteristic bands which indicates the Stark effect only. The paramagnetic cyanides exhibit, in addition to these characteristic bands, other bands which indicate the result of deformation in addition to the Stark effect. Similarly in $Na_2[Fe(CN)_5NO]$ neither the bands correlated to co-ordinated nitrogen nor those produced by the co-ordinated CN-groups show the effect of deformation ; the Stark effect is, however, strongly marked, since the whole absorption is much more diffuse in the presence of foreign ions.

It may therefore be concluded that these salts and the cobaltic ammines behave similarly to the diamagnetic cyanides, indicating that the presence of foreign ions produces mainly a molecular Stark effect with only slight deformations of the molecules concerned. We have, however, to add a few words about those complex salts on which mea-surements were made in the presence of $CO_3$ ions. Here the appearance of new bands indicates the introduction of the $CO_3$ ion into the first sphere of the complex salt. Probably one (or more) of the $(NH_3)$ molecules or of the negative ions which are co-ordinated to the cobalt can be exchanged against $CO_3$ ions. So in the solution the absorption spectra indicate an equilibrium between

$$[CO(NH_3)_6]^{+++} \text{ and } [CO(NH_3)_5CO_3]^+, \text{ etc.}$$
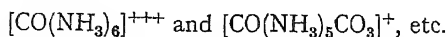
We may consider now the other two salts, $K_2[PtCl_4]$ and $Na_2[RhCl_6]$. Here the complex ion is a negative ion and we should therefore expect that positive ions would influence the absorption maxima, whereas negative ions would have no effect since they cannot approach the com-plex itself. Actually, however, quite the opposite type of behaviour is observed. The absorption curves in the presence of KCl and NaCl show only small shift due to the Stark effect ; but a large displacement

occurs owing to the presence of other negative ions than chlorine. It is also noticed that the maxima are displaced quite differently in the presence of the foreign ions. The absorption maxima in the ultra-violet are very approximately constant in their wave-lengths but widely different in their log $K$ values. The maxima in the visible region are shifted towards the longer wave-length by the influence of negative ions.

Exactly the same behaviour was observed in (III.) in the case of $K_2[PdCl_4]$ in the presence of KBr and for $Na_2[PtCl_6]$ and $H_2[PtCl_6]$. Hantzsch[2] found a considerable displacement of the absorption curve when dissolved in different alcohols.

As we have found now the same phenomenon in $K_2PdCl_4$, $K_2[PtCl_6]$, and $Na_3[RhCl_6]$, we may say that apparently this does not depend either on the co-ordination number (as it is observed with the numbers four and six), or on the central metal ion, but on the fact that all the co-ordinated ions are halogen ions. In this case the strong change of the curves occurs if we introduce negative ions in the solution other than the co-ordinated ones. As in (III.) we may still take it as a possible explanation that the presence of free Br ions in the solution induces an equilibrium such as $[PtCl_6]^{--} \longleftrightarrow [PtCl_4Br_2]^{--}$, but this will hardly hold good if the free negative ion is $SO_4$. In spite of the different nature of the co-ordinated ion and the free ion, the displacement of the curve is less pronounced in this case, and, whereas the bromine ion produces a shift of the whole curve towards longer wave-length, the $SO_4$ ion has just the opposite effect.

To understand this behaviour, we have to remember certain results of previous investigations. From observations of the optical properties of co-ordinated compounds we have come to the conclusion that co-ordinated molecules may exhibit quite different types of linkage. We consider here only those which exist as chemical individuals in solutions, taking it for granted that in the crystal the geometrical properties of the lattice and the electrostatic forces between the molecules may produce quite different co-ordination numbers, such as $4\frac{1}{2}$ or $5\frac{1}{2}$ instead of 4 and 6.

The absorption curves of forty complex salts have been measured, twelve of which were also examined in different solvents. One distinct type is represented by the ammino salts and cyanides of the transition elements like Cr, Mn, Fe, Co, Ni, Os, Ir, etc. The spectrum shows bands of selective absorption which are neither due to the separated metallic ion nor to the co-ordinated groups or molecules alone. Hence there exist in such a molecule new electronic levels indicating some kind of non-electrostatic linkage (cf. I., II., III.). These salts may be termed " genuine complex salts."[3]

In those cyanides in which the central ion exhibits the co-ordination number six, there occurs in the Raman effect (in addition to the inner vibrational frequency of the co-ordinated group) a frequency correlated to the vibration of the group against the central ion as direct evidence of a non-heteropolar bond. This frequency, however, is absent in certain complex salts such as $K_2[Ni(CN)_4]$ and $K[Ni(CN)_3]$, with lower co-ordination number (cf. IV.). Furthermore, the absorption spectra of the tetracyanides of nickel, palladium and platinum are less characteristic than those of the hexacyanides of the other atoms (cf. I.).

[2] Z. physik. Chem., 84, 321, 1913.
[3] Cf. H. Lessheim, Jul. Meyer and R. Samuel, Z. Physik, 43, 199, 1927; Z. anorg. Chem., 165, 253, 1927.

In the case of the hexahydrates [4] we find direct connection between the absorption spectrum and the term differences of the free metal ion, *e.g.* $Cr^{+++}$, $Cr^{++}$, etc., indicating that free metal ions and unstable molecules such as $(CrCl)^{++}$, etc., are formed, whereas the co-ordinated water molecules do not influence the absorption spectrum (*cf.* V.). They are probably bound only as dipole associations, and cannot be compared with the hexammines or cyanides.

Moreover, the salts of the type $K_2[BeF_4]$ or $K_2[TiF_6]$, in which the metal exhibits its maximal valency, do not show the characteristic selective absorption produced by co-ordination in the genuine complex molecules. They clearly belong to quite another type. This is in agreement with the investigations of Ulith and his co-workers [5] who have shown that the molecular associations formed by the trihalides of aluminium and boron and the dihalides of beryllium combine on account of electrostatic forces only. To our mind, also, the linkage between beryllium fluoride and the two fluorine ions is merely of an electrostatic nature, the more so since the occurrence of such molecules is mainly observed in the first periods where the electrostatic forces are at their strongest owing to the small atomic dimensions of these elements.[6]

In the salts in question, in which chlorine ions are co-ordinated to positive ions of the transition elements, there occur bands of selective absorption indicating a non-electrostatic linkage. On the other hand, there is some evidence of a facile exchange of some of the chlorine ions with bromine ions, and for an extremely strong deformation of the negative co-ordinated complex just in a negative field. This behaviour might be explained if we assume that all halogen ions are not linked in the same manner. If two of the four or six chlorine ions are bound by electrostatic forces only, then it is clear that they are capable of being easily exchanged and this explains why such substances do not follow Beer-Lambert's Law, and why negative ions come so near to the negatively charged centre of absorption that their influence becomes extremely strong. There seem to be some features in the chemical behaviour supporting such a distinction between the linkages. Thus the number of isomeric molecules is smaller than it should be and its isomeric conditions are not changed in the process of transition from a molecule having divalent platinum with co-ordination number four to one having tetravalent platinum with co-ordination number six. It is not yet possible to come to definite conclusions in the present state of investigation, but the behaviour of these salts in the presence of foreign ions is so different from that of other genuine complex salts, that we are inclined to adopt this assumption for the meantime as a working hypothesis. It is certain, however, that even where the ions exist as chemical individuals in solution and where the co-ordination number is the same, quite different physical mechanisms are responsible for the existence of these molecules, and any attempt to develop a theory of co-ordination on the basis of atomic physics will have to take account of this fact.

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*The Muslim University,*
*Aligarh.*

[4] There is no evidence for the assumption that we have hexahydrates in solution. The co-ordination number six (and some others) is proved only in crystals with definite geometrical conditions.

[5] H. Ulith and W. Nespital, *Z. angew. Chem.*, 44, 750, 1931 ; W. Nespital, *Z. physik. Chem.*, 16B, 153, 1932.

[6] *Cf.* R. F. Hunter and R. Samuel, *J.C.S.* (1934), 1180.

# THE ULTRA-VIOLET ABSORPTION SPECTRA OF THE STANNIC HALIDES IN VARIOUS SOLVENTS.

By Margaret I. Grant.

Previous work has shown that a solution of stannic iodide in ethyl alcohol gives an absorption curve very similar to that of a solution of iodine in ethyl alcohol. This seems to support Scheibe's view that absorptions of this type are determined only by the halogen atom present.[1] It was the original aim of this research to find out if this similarity held for other solvents.

Many lines of evidence indicate that substances are solvated in solution, *i.e.*, each molecule is surrounded by a sheath of solvent molecules which is held, more or less firmly, by some kind of electronic interaction between the dipole of the solute and that of the solvent. This interaction results in a deformation of the electron systems of the molecules concerned, and for any one solute the interaction (and deformation) increases with increasing dipole strength of the solvent. As the absorption of a substance is due to energy changes in its electron system,[1] it is to be expected that change in the dielectric constant of the solvent would produce corresponding changes in absorption. For solvents such as hexane, which have very small dipoles, the deformation of the electron system of the dissolved molecule is very slight, so that the absorption of a substance dissolved in hexane may be taken as closely approximating to that of the non-deformed unsolvated molecule. For this reason hexane was the first solvent used in this research.

A solution of iodine in hexane is purple, and has an absorption curve similar to that of iodine vapour (Fig. 1, curve 2). Stannic iodide in hexane gives a yellow solution with an absorption curve similar to that of iodine in ethyl alcohol (Fig. 1, curve 1), but it was found that this solution did not obey Beer's Law, and on standing the colour slowly changed to brown and later to purple, and a white deposit formed. This solid was filtered off, washed thoroughly with hexane, and on examination was found to contain tin but no iodine. This pointed to the stannic iodide having decomposed with the formation of free iodine ; to test this, the purple solution was shaken up with finely divided metallic silver, the solution became colourless and a yellow deposit (which proved to be silver iodide) formed on the surface of the silver.

Means were then sought by which to prevent the decomposition of the stannic iodide, and it was found that if allowed to stand over finely-divided metallic tin the solution did not darken on standing, although a white deposit gradually formed. This solution gave an absorption curve (Fig. 2, curve 4) which obeyed Beer's Law within the limits used.

A solution of iodine in hexane was then shaken up with finely divided tin, and it was observed that the colour gradually changed from violet through brown to pale yellow ; the final solution gave the same curve as that of stannic iodide in hexane over tin (Fig. 2, curve 4) if in calculating the concentration of iodine the molecule is taken as $I_4$, and obeyed Beer's

[1] Scheibe, *Z. Elektrochemie*, **34**, 497, 1928.

Law. Tin and iodine combine directly with the formation of stannic iodide, so this curve may be taken as the true curve for stannic iodide in hexane.

It seemed probable that the observed similarity between the curves for
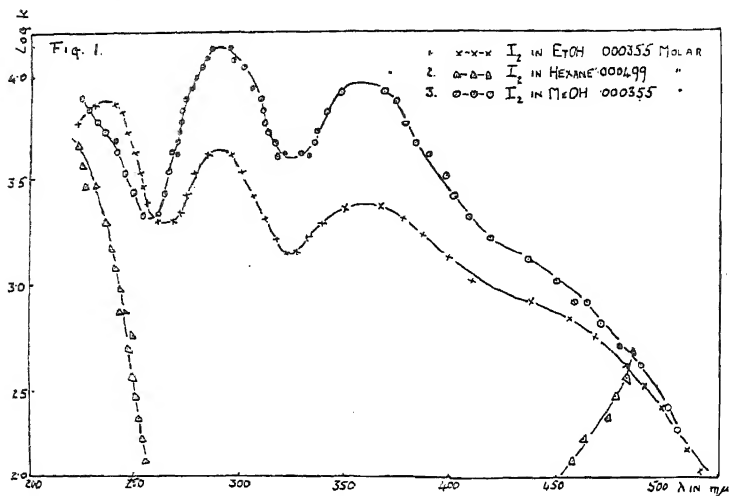


stannic iodide and iodine in ethyl alcohol was due to the slow decomposition of the stannic iodide with the liberation of free iodine, so a solution of stannic iodide in ethyl alcohol was made up and allowed to stand over metallic tin. This solution was pale yellow and gave a curve (Fig. 2,
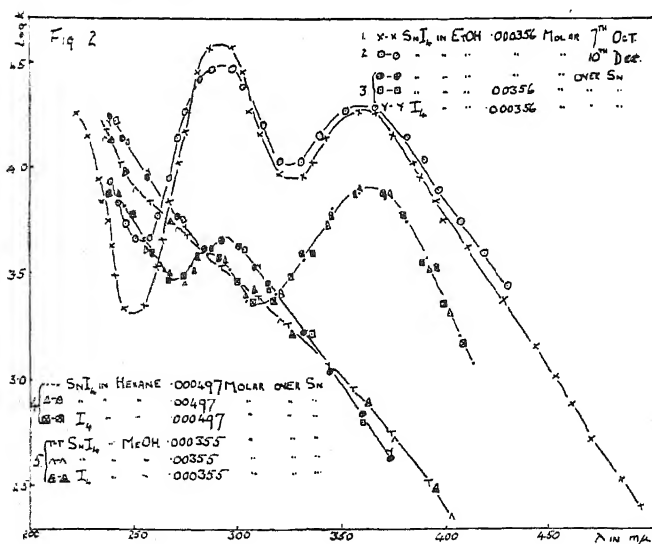


curve 3) quite different from that of iodine in ethyl alcohol (Fig. 1, curve 1) and obeyed Beer's Law. Stannic iodide in ethyl alcohol with no metallic tin present had an absorption curve which changed on standing (Fig. 2, curves 1 and 2). Ethyl alcohol was allowed to stand over tin for a month,

but no absorption was observed.   A solution of iodine in ethyl alcohol was shaken up with metallic tin and the colour gradually changed from dark brown to pale yellow ; the resulting solution gave the same curve as that of stannic iodide in ethyl alcohol if in calculating the concentration of iodine the molecule is taken as $I_4$ (Fig. 2, curve 3) ; this solution also obeyed Beer's Law.   This curve may be taken as the true curve for stannic iodide in ethyl alcohol.

Similarly stannic iodide in methyl alcohol in the presence of metallic tin gave a curve (Fig. 2, curve 5) quite different from that of iodine in methyl alcohol without tin (Fig. 1, curve 3), but the same as that for iodine in methyl alcohol over tin.

A solution of stannic iodide in acetonitrile over tin decomposed too rapidly under the action of the ultra-violet light for any curve to be obtained.

As the curves for stannic iodide in ethyl alcohol and in hexane are so different a series of solutions of stannic iodide in hexane containing varying amounts of ethyl alcohol over metallic tin was examined in an attempt to trace the transition from one curve to the other.   With small amounts of
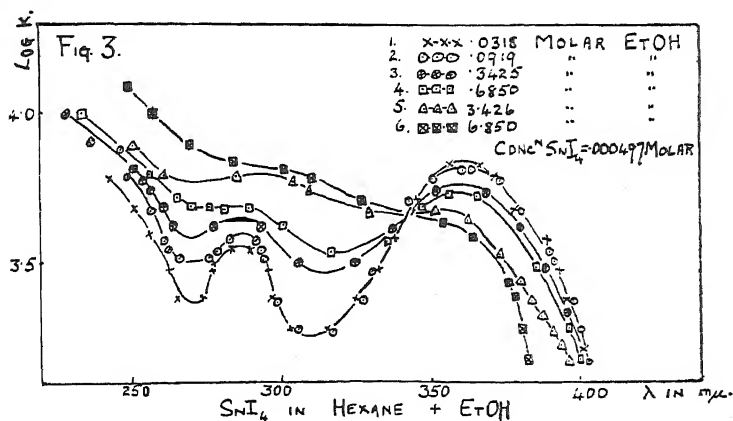


Fig. 3.

ethyl alcohol (0·0318 and 0·09 molar) the curve differed very little from that of stannic iodide in hexane over tin (Fig. 3, curves 1 and 2).   But with increasing amount of alcohol (Fig. 3, curves 3-6) the short-wave maximum rose and shifted towards the red, while the long-wave maximum fell and shifted towards the ultra-violet, the curve gradually flattening out until at length both maxima practically disappeared.   All the curves passed through the same point (within the limits of experimental error) at about $\lambda = 343$ m$\mu$ and log $K = 3·66$.

A solution of stannic bromide in hexane (which is colourless) was examined, and it was found that, even in the presence of metallic tin, the absorption altered with time (Fig. 4, curves 1-3).   The maximum wavelength did not change, but log $K_{max.}$ gradually decreased.

The absorption of stannic bromide in methyl alcohol over tin also changed with time (Fig. 5, curves 1, 2, 4).   Both in the case of hexane and methyl alcohol a white deposit formed when the solution was allowed to stand, but the solution itself remained colourless.   Stannous bromide in methyl alcohol has a curve (Fig. 5, curve 3) similar to that of stannic bromide in methyl alcohol, but further towards the ultra-violet.   Stannous bromide is insoluble in hexane.

## Procedure.

The absorption curves referred to were obtained by plotting the logarithm of the absorption coefficient against the corresponding wave-length. The absorption coefficient is defined by the Beer-Lambert Law for the absorption of light by an absorbing medium :—

$$\log_{10} \frac{I_0}{I} = Kcd,$$

where $I_0$ is the intensity of the beam of monochromatic light, $I$ is the intensity of the same beam after passing through a length $d$ cm. of the absorbing medium, $c$ is the concentration in mols. per litre of the absorbing substance, and $K$ the absorption coefficient.

The apparatus used in measuring $K$ consisted of a Bellingham and
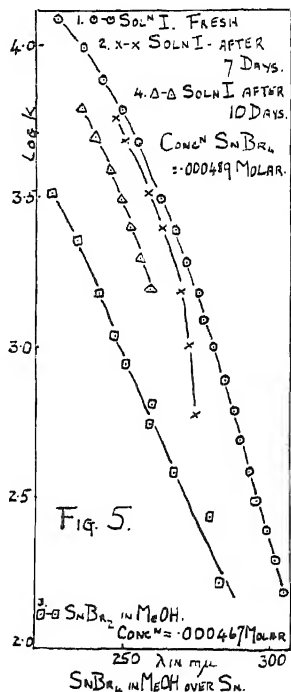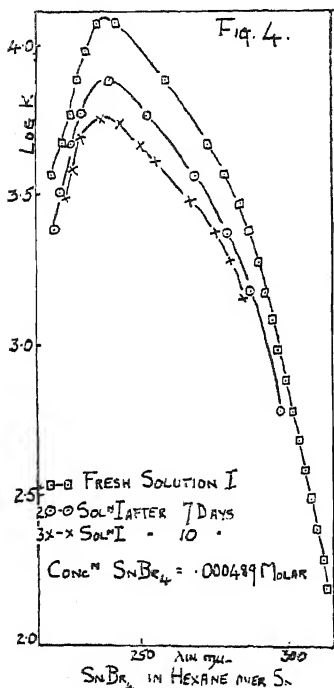


Stanley sector photometer in conjunction with a Bellingham and Stanley " medium " quartz spectrograph (plates 10 × 4 ins.). The source of ultra-violet light was an iron-spark. Ilford " Thin-film Half-tone " plates were used for wave-lengths less than 400 m$\mu$ and " Zenith Super-Sensitive " (650 H and D) plates for longer wave-lengths.

All the solutions were kept under a blackened bell-jar as they tended to decompose if exposed to bright sunlight ; for the same reason as short exposures as possible were used and the solution in the cell was changed before each exposure.

### Materials.

Stannic Iodide—Prepared by the method of McDermott from metallic tin and A.R. iodine dissolved in carbon tetra-chloride.[2]

[2] McDermott, *J. Am. Chem. Soc.*, **33**, 1963, 1911.

Stannic Bromide—Prepared from tin and bromine by the method of Lorenz.[3]

Stannous Bromide—By the method of Butler and Hamilton by passing pure dry hydrogen bromide into dry ether standing over tin.   The hydrogen bromide was prepared by dropping bromine onto benzene.[4]

Hexane—The " specially purified for spectroscopy " product of the B.D.H.

Methyl Alcohol—Prepared from absolute methyl alcohol by drying with magnesium, refluxing and distilling.[5]

Ethyl Alcohol—Prepared from absolute ethyl alcohol by refluxing with iodine ;  the alcohol was distilled off and the excess iodine removed by refluxing with magnesium and the alcohol was then redistilled.

Acetonitrile—A.R. acetonitrile was dehydrated over phosphorus pentoxide and redistilled.[6]

## Discussion.

### 1. Stannic Iodide in Hexane.

Hexane is a practically non-polar solvent, so that its molecules have little or no deforming effect on the electron systems of the molecules of substances dissolved in it.   Hence the molecules of stannic iodide are merely dissolved in the hexane and not solvated (*i.e.*, not associated with solvent molecules) to any appreciable extent, and the absorption curve in hexane is that for stannic iodide in the normal undeformed state.   This curve shows two maxima (1) at $\lambda = 365$ m$\mu$ and (2) at $\lambda = 285$ m$\mu$. The difference in these wave-lengths corresponds to a wave-number difference of $7710$ cm.$^{-1}$ which is approximately equal to the wave-number difference between a normal and an excited iodine atom, *i.e.*, $8000$ cm.$^{-1}$   It seems, therefore, that the stannic iodide molecule absorbs radiation at $\lambda = 365$ m$\mu$ and dissociates giving an unexcited iodine atom. At $\lambda = 285$ m$\mu$ the stannic iodide molecule now absorbs just the right amount of energy to give an iodine atom in the excited state.

### 2. Stannic Iodide in Ethyl Alcohol.

In the case of the solution of stannic iodide in ethyl alcohol, the electron system of the stannic iodide molecule is greatly deformed by the strong dipole of the solvent, and now only energy corresponding to $\lambda = 295$ m$\mu$ is required to do the work which in hexane required corresponding to $\lambda = 285$ m$\mu$.   According to Scheibe [7] the shift of the maximum. at $\lambda = 285$ m$\mu$ in hexane to 295 m$\mu$ in ethyl alcohol indicates that the chromophore group is negative, because a negative chromophore attracts the positive end of the solvent dipole towards it, thus it is surrounded by a positive field, less energy is required for the electron spring, and the maximum shifts towards the red.

Also, the deformed molecule is unable to absorb radiation at $\lambda = 365$ m$\mu$ as no maximum appears at that wave-length on the curve for stannic iodide in ethyl alcohol.   The ability to absorb radiation is a question of resonance, and the natural frequencies of the deformed molecule do not respond to $\lambda = 365$ m$\mu$ although radiation of that wave-length has enough energy to dissociate the molecule ; *cf.* hydrogen can be dissociated by

[3] Lorenz, *Z. anorg. Chem.*, **9**, 366, 1895.
[4] Butler and Hamilton, *J.C.S.*, 2283, 1932.
[5] Bjerrum, *Ber.*, **56**, 894, 1923.
[6] Lederle, *Z. physik. Chem.*, **10B**, 121, 1930.
[7] Scheibe, *Ber.*, **58**, 586, 1925.

radiation of wave-length 254 m$\mu$ as regards energy but it does not absorb at that wave-length. Supposing stannic iodide dissolved in alcohol but was not solvated, then the $\lambda = 365$ m$\mu$ maximum would still appear, possibly displaced towards the red.

According to Chatelet [8] the brown colour of some solutions of iodine is due to solvated iodine, the brown transmission region being equivalent to the near ultra-violet region of transparency in the vapour (or in hexane).

### 3. Stannic Iodide in Methyl Alcohol.

This curve shows neither of the two maxima of the stannic iodide in hexane curve. Methyl alcohol has a greater dipole moment than ethyl alcohol, so that the electron systems of the dissolved stannic iodide molecules are even more deformed, and the distribution of the radiation absorbed by them differs from that when ethyl alcohol is the solvent so that a different absorption curve would be expected and the results obtained fulfil this expectation.

### 4. Stannic Iodide in Hexane and Ethyl Alcohol.

When increasing amounts of ethyl alcohol are added to the hexane used as solvent, the dissolved stannic iodide molecules gradually become



Fig. 6.

solvated. The curves all pass through one point so that an equilibrium exists between the two states of stannic iodide (solvated and unsolvated) in the solution.[9] Only the unsolvated molecule absorbs to any great extent at $\lambda = 365$ m$\mu$; on the addition of ethyl alcohol some of the stannic iodide molecules become solvated, so that there are fewer in the state capable of absorbing the radiation at $\lambda = 365$ m$\mu$ and the value of log $K$ at that point falls. The degree of solvation can be calculated as follows :—
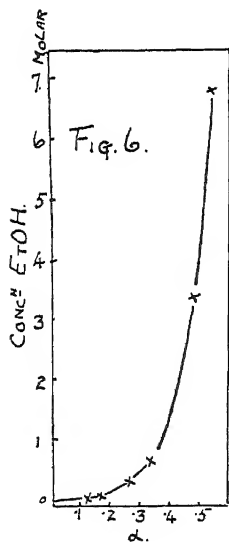
Let $\alpha$ = degree of solvation.

,, $c$ = total molar concentration of stannic iodide.

$\therefore$ conc. of solvated molecules = $\alpha c$.

conc. of unsolvated molecules = $(1 - \alpha)c$.

Let $K_m$ = measured absorption coefficient at $\lambda = 365$ m$\mu$.

,, $K_1$ = absorption coefficient for unsolvated SnI$_4$ at $\lambda = 365$ m$\mu$.

,, $K_2$ = absorption coefficient for solvated SnI$_4$ at $\lambda = 365$ m$\mu$.

(K$_1$ and K$_2$ are obtained from the curves for stannic iodide in hexane and in ethyl alcohol respectively).

$$K_m c = K_2 \alpha c + K_1 c (1 - \alpha).$$
$$K_m = K_2 \alpha + K_1 (1 - \alpha).$$

This equation gives $\alpha$ for each concentration of ethyl alcohol. If $\alpha$ is plotted against the concentration of ethyl alcohol a smooth curve is obtained (Fig. 6).

[8] Chatelet, *Ann. Chim.*, **11**, 1, 1934.
[9] Weigert, *Optische Methoden der Chimie*, p. 184.

The curve for stannic iodide in ethyl alcohol and hexane is the resultant of the curves for stannic iodide in ethyl alcohol and in hexane ; on increasing the amount of ethyl alcohol, more and more stannic iodide molecules become solvated and the ethyl alcohol curve gradually predominates. At $\lambda = 285$ m$\mu$ the solvated molecule has a greater absorption (log $K = 3\cdot67$ as against log $K = 3\cdot60$) at $\lambda = 365$ m$\mu$ a much smaller absorption (log $K = 2\cdot76$ as against log $K = 3\cdot90$) than the unsolvated molecule, so that on addition of ethyl alcohol to the hexane solution the curve rises in the region of $\lambda = 285$ m$\mu$ and falls in the region of $\lambda = 365$ m$\mu$. Also as the maximum for the completely solvated stannic iodide (ethyl alcohol curve) lies between the two maxima for the unsolvated molecule (hexane curve) the $\lambda = 285$ m$\mu$ maximum shifts towards the red and the $\lambda = 365$ m$\mu$ maximum towards the ultra-violet on the addition of ethyl alcohol to the hexane.

An attempt was made to obtain similar series with methyl alcohol and acetonitrile instead of ethyl alcohol but was unsuccessful owing to the immiscibility of these solvents with hexane.

## 5. Comparison of Behaviour of the Curves for Stannic Iodide and Stannic Bromide.

Stannic iodide and stannic bromide being very similar compounds it might have been expected that their absorption curves would behave in a similar manner under the same influence, but we see from the above results that this is not the case. Solutions of stannic iodide standing over metallic tin are stable and obey Beer's Law, while if no tin is present the solution gradually turns brown. On the other hand, solutions of stannic bromide remain colourless but their absorption changes with time whether metallic tin is present or not. In the case of both halides a white deposit forms slowly.

The stannic halides are fairly readily hydrolysed by water,[10] and the following explanation of the above observations is based on this fact.

The solvent, however carefully dried, absorbs moisture from the air whenever the stopper of the flask is removed and from the surfaces of the various vessels used. These traces of moisture gradually hydrolyse the stannic halide with the eventual formation of stannic hydroxide which appears as the white deposit observed. Probably various oxyhalides are formed as intermediate products during the hydrolysis, but they in their turn are hydrolysed until finally stannic hydroxide is reached. The complete reaction may be represented by the equation

$$SnX_4 + 4H_2O = Sn(OH)_4 + 4HX$$
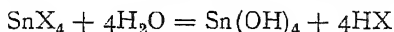
In the case of stannic iodide the hydrogen iodide liberated is unstable (especially in sunlight) [11] and readily forms free iodine which produces the brown coloration of the solution ; iodine, however, reacts with metallic tin with the formation of stannic iodide, so that, in the presence of tin, the iodine is taken up as soon as it is formed, and the concentration of stannic iodide in the solution remains constant, and the equivalent of the tin that goes into solution as stannic iodide is deposited as stannic hydroxide.

Hydrogen bromide, on the other hand, does not readily decompose with the formation of free bromine so the solution remains colourless, but hydrogen bromide reacts with metallic tin to form stannous bromide.

[10] Pfeiffer, *Ber.*, **38**, 2466, 1905.          [11] Mellor, *Inorg. and Theoret. Chem.*

Thus in solutions of stannic bromide the concentration of stannic bromide gradually decreases, and that of stannous bromide increases (in solvents in which it is soluble) as the hydrolysis proceeds, so that the maximum on the curve for stannic bromide gradually falls.  Stannous bromide is insoluble in hexane but soluble in methyl alcohol so that with the former solvent there is no shift of the maximum wave-length, but with the latter solvent the curve gradually moves towards that for stannous bromide, *i.e.*, towards the ultra-violet.

The two reactions may be represented diagrammatically thus :—

$$SnI_4 \xrightarrow{H_2O} Sn(OH)_4 + HI$$

$$Sn$$

$$I_2$$

$$SnBr_4 \xrightarrow{H_2O} Sn(OH)_4 + HBr$$
$$\downarrow Sn$$
$$SnBr_2$$
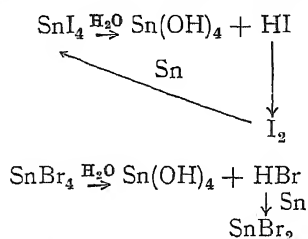
## Summary.

The effect of change of solvent on the absorption of stannic iodide and stannic bromide is examined and discussed.   A difference in the behaviour of solutions of stannic iodide and of stannic bromide is observed, and an explanation of this put forward.

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# THE KINETICS OF THE DECOMPOSITION OF NICKEL CARBONYL.

By C. E. H. Bawn.

Nickel carbonyl is decomposed on heating into nickel and carbon monoxide according to

$$Ni(CO)_4 \rightleftharpoons Ni + 4CO \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

The kinetics of the formation of nickel carbonyl by this reaction and a study of the equilibrium relationships has been made by Mittasch,[1] who also concluded that the decomposition was approximately a first order process.   In connection with other investigations it was necessary to have a more complete knowledge of this reaction, and in the present investigation it has been found that the decomposition of nickel carbonyl

[1] *Z. physik. Chem.*, **40**, 1, 1902.

vapour in nickel coated glass vessels is inhibited by the carbon monoxide formed, and that the reaction follows closely the relationship

$$dx/dt = k \cdot \text{Ni(CO)}_4 / 1 + k^1 \cdot \text{CO} \qquad . \qquad . \qquad . \quad (2)$$

## Experimental.

The reaction was followed by observing the increase in pressure which accompanied the decomposition. The reaction vessel was suspended in an electrically-heated oil bath, the temperature of which could be regulated by a hand-operated resistance. The temperature was measured by means of a mercury thermometer, and was constant to within $0.05°$ C. during an experiment. The pressure was measured by a capillary mercury mano-meter attached directly to the reaction vessel. The volume of the mano-meter and other dead space was less than 3 per cent. of the total volume of the reaction system. Nickel carbonyl was stored in a large glass vessel maintained at constant temperature by immersion in a water bath. The volume of this vessel was accurately calibrated and the pressure of nickel carbonyl vapour in it could be read by a second capillary manometer. The system was evacuated by means of a mercury vapour pump backed by a hyvac oil pump.

A sample of nickel carbonyl which had been obtained from the Mond Nickel Company was used. It was purified from carbon monoxide by condensing in a liquid air-cooled vessel and evacuating, and was finally distilled from $-20°$ to $-190°$ C. before use. Carbon monoxide was pre-pared by dropping formic acid on to concentrated sulphuric acid. It was purified by passage through caustic potash and was dried over phosphoric oxide.

The experimental procedure was as follows : Nickel carbonyl was allowed to enter the reaction vessel from the storage vessel by opening for a period of three seconds a small tap connecting the two. A stop watch started at two seconds gave the initial time of the experiment. From a knowledge of the change in pressure in the storage bulb, its volume and the volume of the reaction vessel, it was possible to calculate, by the use of an experimentally determined pressure-temperature calibration curve, the initial pressure in the reaction vessel. This was necessary, since at the temperatures employed the decomposition was so rapid that it was im-possible to determine the initial pressure by extrapolation. The rate of decomposition was followed by reading the pressure every five seconds up to the half minute, and every fifteen seconds afterwards. For the carrying out of these operations two persons were necessary, and the author wishes to express his thanks to K. Tomlinson and H. Alcock for valuable assistance in this respect.

## Results.

In accordance with the observations of Mittasch[1] it was found that nickel carbonyl vapour decomposed very rapidly at $105°$ C., and at these temperatures more than 90 per cent. of the vapour was decomposed within a comparatively short period of time. At lower temperatures an equili-brium is set up in accordance with (I). The experiments to be described were carried out at temperatures of $100°$ to $128°$ C., and under these conditions the reversible change is negligible. Also, blank experiments at $118°$ C., using carbon monoxide gas, showed that there was no measureable loss of gas by adsorption at the nickel-covered surface. The curves given in Fig. 1 show the course of the reaction at a series of pressures and two temperatures. Determination of the initial rates of reaction from the slope of the pressure time curve showed that the order of the reaction was apparently less than one. It has been found that the relationship

$$dx/dt = \frac{k \cdot \text{Ni(CO)}_4}{1 + k' \cdot \text{(CO)}}.$$

fits the results of all the series of experiments. This was shown in the following manner : if the initial concentration of the nickel carbonyl is $a$, and $x$ is the amount of decomposition at time $t$, then

$$dx/dt = \frac{k(a - x)}{1 + k'_1 x}.$$

Integrating and introducing the condition that when $t = 0$, $x = 0$, one obtains :—

$$k = \frac{1}{t} \log \frac{a}{a - x} + \frac{ak'_1}{t} \log \frac{a}{a - x} - \frac{1}{t} k'_1 x,$$

and this reduces to

$$k_{\text{uni}} = k'_0 + \frac{k''_0 x}{t}$$

where $k_{\text{uni}}$ is the calculated unimolecular constant and $k'_0$ and $k''_0$ are constants. If this equation is valid, the plot of $k_{\text{uni}}$ against $x/t$ should give
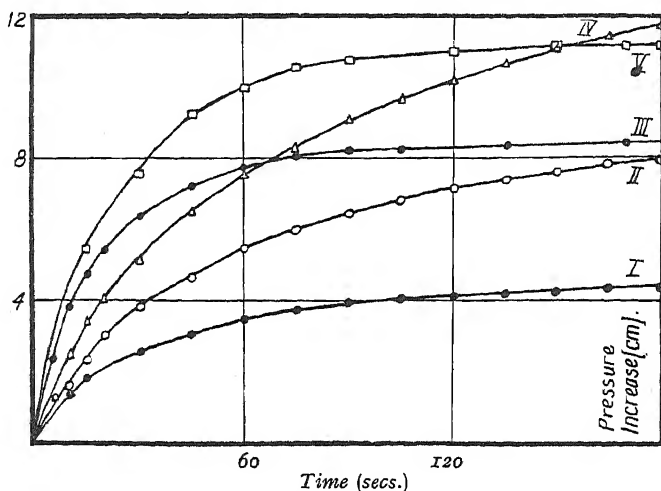


FIG. 1.—Influence of Pressure.
Curves I, II and III. Temperature 105° C. Initial Pressures 1·74, 3·55 and 6·36 cms.
Curves IV and V. Temperature 118·6° C. Initial Pressures 3·00 and 3·94 cms.

a straight line the intercept of which on the $x/t$ axis should be constant, but with slope varying with the initial concentration. Some typical curves verifying this law are shown in Fig. 2.

### Effect of Surface.

After a few experiments the reaction vessel became coated with a thin film of nickel which had a brilliant appearance. Observations on the nature of this film showed that after a large number of experiments had been performed in the vessel, the nickel was no longer deposited as a metallic coating but as an apparent fine powder which soon formed a thick layer. Simultaneously, with the formation of this layer a marked increase in reaction velocity was observed. This was attributed to the occurrence of a surface reaction. However, if the reaction vessel was replaced by a new one, the original rate conditions were obtained. It was thus necessary to limit the number of experiments which could be carried out in any single bulb, and it was found that no disturbing surface effects were observed during the first thirty experiments. The existence of this surface reaction was confirmed by experiments using two similar bulbs, one of which was empty whilst the other was packed with a large number of glass tubes.

This corresponded to approximately 8·4 times increase in surface. The results of two sets of experiments are given in Fig. 3. If it is assumed that the original surface had the same catalytic activity as the added surface, then at 118° C. the wall reaction would amount to about 20 per cent. of the total measured reaction. Up to 60 per cent. decomposition the same rate law was obeyed as in the empty vessels (see Fig. 2, curves 1 and 2). The falling off during the latter part of the change was probably due to some secondary surface reaction.

### Influence of Carbon Monoxide.

The relationship which has been found to explain the results indicates that the reaction is inhibited by the carbon monoxide formed during the reaction, and thus it would be expected that carbon monoxide added
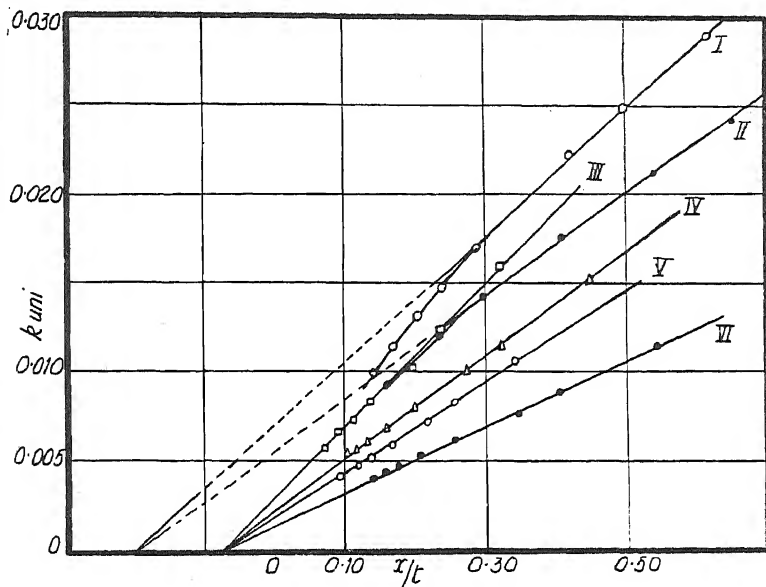


FIG. 2.

Curves I. and II. $\begin{cases} Ni(CO)_4 \\ Packed\ Vessel. \end{cases}$ Temperature 119° C.
   III. ,, V.  $Ni(CO)_4 + 40$ per cent. CO. Temperature 108·2° C.
   IV. ,, VI.  $Ni(CO)_4$. Temperature 108·2° C.
Initial Pressures :—
   I. 6·55 cms. $Ni(CO)_4$. II. 7·66 cms. $Ni(CO)_4$. III. 3·79 cms. $Ni(CO)_4$.
   IV. 5·61 cms. $Ni(CO)_4$. V. 5·93 cms. $Ni(CO)_4$. VI. 8·85 cms. $Ni(CO)_4$.

initially would exert a similar inhibiting effect. This was confirmed, as shown in Fig. 4. In these experiments a nickel carbonyl-carbon monoxide mixture was used. It was also shown that the product of the reaction (carbon monoxide made by the decomposition of nickel carbonyl at 130° C.) had the same influence as carbon monoxide made as previously described. In the presence of excess carbon monoxide equation (3) is modified to :—

$$k_{uni} (1 + k'_1 p + ak'_1) = k + \frac{1}{t}k'_1 x,$$

where $p$ is the initial pressure of the carbon monoxide. In this case the plot of log $k_{uni}$ against $x/t$ will give a straight line, with the same intercept as obtained in the decomposition of pure nickel carbonyl, but with a different slope. The validity of this relationship is evident from Fig. 2.
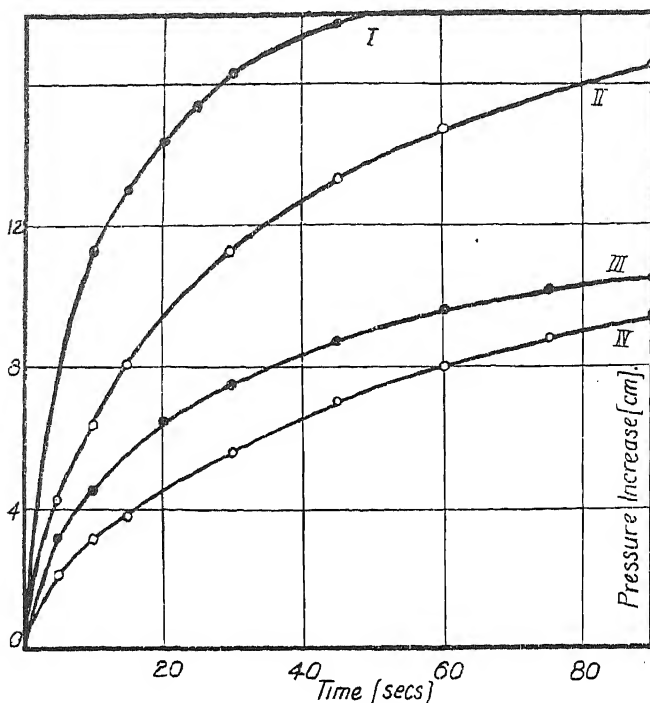
Fig. 3.—Influence of Surface.
Curves I. and II.   Temperature 118·6° C.   Initial Pressure 6·15 cms.
I. Packed Vessel.   II. Unpacked Vessel.
Curves III. and IV.   Temperature 108·2° C.   Initial Pressure 7·38 cms.
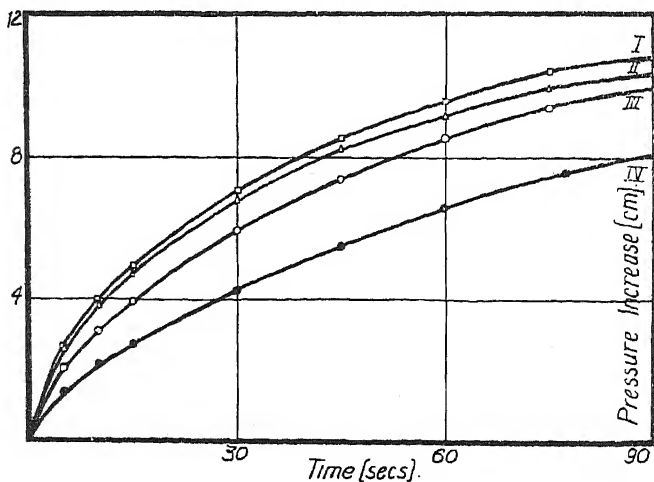III. Packed Vessel.   IV. Unpacked Vessel.



Fig. 4.—Influence of Carbon Monoxide.   Temperature 108·1° C.
I. Pressure Ni(CO)$_4$ 5·61 cms.        II. Pressure Ni(CO)$_4$ 5·31 cms.
III. Pressure 5·93 + 40 per cent. CO.   IV. Pressure 5·39 + 55 per cent. CO.
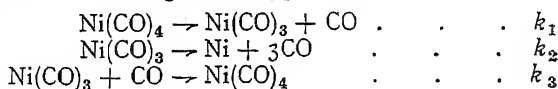
**Temperature Coefficient.**

A determination of the temperature coefficient and the activation energy has been made. The average value of the activation energy for two series of results as determined from the log $\frac{dx}{dt}$ (initial) $-\frac{1}{T}$ curve is 10,250 cals.

## Oxidation of Nickel Carbonyl.

Some preliminary results on the oxidation of nickel carbonyl have been obtained. The experimental procedure was to admit known amounts of oxygen from a gas burette into the nickel carbonyl contained in the reaction vessel. It was found, using a constant pressure of nickel carbonyl, that if the oxygen pressure exceeded a certain critical value explosion occurred, but below this pressure no measureable reaction was observed. The explosion was preceded by a marked induction period, which varied from a few seconds to more than a minute in successive experiments. Although the phenomena have not been investigated in detail, the explosion appears to exhibit the characteristics of a branching chain reaction. The marked variations in the induction period and in the occurrence of explosion can be attributed to the change in the nature of the surface from which the reaction chains are initiated.

## Discussion.

The most important fact obtained from these experiments is that the reaction which is partly homogeneous and partly heterogeneous, gives the same rate law independent of the presence of added surface or excess carbon monoxide. Therefore, both the surface and gas reactions are inhibited by the carbon monoxide formed. The decomposition occurs principally in the gas phase, and the observed relationship can be readily explained if it is assumed that decomposition involves more than one stage. We can assume the following series of processes :—

$$Ni(CO)_4 \rightarrow Ni(CO)_3 + CO \quad . \qquad . \qquad . \quad k_1$$
$$Ni(CO)_3 \rightarrow Ni + 3CO \qquad . \qquad . \qquad . \quad k_2$$
$$Ni(CO)_3 + CO \rightarrow Ni(CO)_4 \qquad . \qquad . \qquad . \quad k_3$$

which give the required rate law.

On the other hand, a different mechanism is necessary to explain the inhibiting effect of carbon monoxide on the heterogeneous part of the reaction. In this case the type of reaction is well known, and corresponds to a reaction in which the nickel carbonyl is weakly adsorbed compared to the much greater adsorption of the carbon monoxide.

In conclusion, the author wishes to express his thanks to A. G. Evans, B.Sc., for some assistance with the experimental work, and to the Imperial Chemical Industries Limited for a grant.

## Summary.

The decomposition of nickel carbonyl vapour in nickel coated glass vessels is partly homogeneous (80 per cent.) and partly heterogeneous (20 per cent.). Both reactions are inhibited by carbon monoxide, and give the same velocity relationship $dx/dt = \dfrac{k_{[Ni(CO)_4]}}{1 + k'_{1[CO]}}$.

A mechanism is suggested for the homogeneous decomposition depending on the dissociation of nickel carbonyl in more than one stage. The inhibition of the heterogeneous reaction is due to the strong adsorption of carbon monoxide on the nickel surface.

*Note Added, 5th December, 1934.*
Since this paper was submitted for publication, a communication by A. P. Garratt and H. W. Thompson has appeared in the *Journal of the Chemical Society* (November, 1934, p. 1822) on the thermal decomposition and oxidation of nickel carbonyl. The results obtained by these authors are in good accord with those presented in this paper, and the mechanism given for the decomposition is the same. These authors also studied the absorption spectrum of $Ni(CO)_4$, and photochemical decomposition, and conclude the primary stage in the later process, *viz.*,

$$Ni(CO)_4 + h\nu \rightarrow Ni(CO)_3 + CO$$
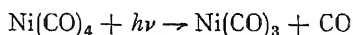
is the same as that of the thermal decomposition.

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  *Manchester.*

# POTASSIUM ETHYL SULPHATE GELS.

## By HERBERT HENSTOCK.

*Received 13th November, 1934.*

Although the solubility of potassium ethyl sulphate in water at 20° is nearly three times that of sodium benzoate and four times that of calcium acetate, it does not, as might have been expected, form aqueous gels nearly so readily as the two latter salts. It seems, therefore, that the quantity of solid material present in a solution is no criterion of the ease of formation of colloids by means of the present methods :[1] but what appears to be of more importance is the capability of the salt to form crystals. Potassium ethyl sulphate crystallises easily from water and many other solvents and is, more often than not, thrown out from its solutions in a crystalline condition, whereas the other two salts, though they can and do crystallise, are of a much more amorphous nature. The gels formed by these salts in methanol solution are formed with the same ease or difficulty respectively, according to their crystal-forming capacities. This deduction is not wholly dependent upon the behaviour of these three salts. Similar conditions have been found to hold amongst those salts, which form gels only in organic solvents, chiefly in the lower, saturated, aliphatic alcohols. Amongst those salts of a more or less amorphous type, so far found to yield colloids easily, might be mentioned sodium formate, calcium propionate, potassium succinate, calcium lactate and lithium acetate, which are not easily crystallisable, but only two of an opposite nature, potassium propionate and potassium *n*-butyrate have been found to gelatinise with equal ease. Sodium acetate, a well-defined crystalline salt, is precipitated, only with difficulty, in a colloidal condition by one or two dispersion media. In fact, of the fifty odd salts of the alkali and alkaline earth metals and ammonium with organic acids already examined for their capabilities of colloid formation, those which have been found to yield colloids are of a more amorphous than crystalline type.

[1] *This Journal*, **29**, 1101, 1933, and **30**, 560, 1934.

## Aqueous Gels.

Since potassium ethyl sulphate is partially hydrolysed by hot water, the solution could not be evaporated by raising the temperature. Accordingly, a weighed portion of the aqueous solution, saturated at 20°, was placed in a vacuous desiccator over sulphuric acid and, after the evaporation of the solvent, the residue was heated at 100° for fifteen minutes and weighed. 166·26 g. of the salt were found to dissolve in 100 g. of water. When ethanol is added to this, the salt is precipitated partly as a white opaque gel and partly as crystals, but if the salt solution is diluted with one-fifth its volume of water, yielding a solution containing 151·14 g. of salt in 100 g. of water at 20°, it will form a white opaque gel containing no crystals. 1·09 g. of this solution requires 2·78 g. (3·5 volumes) of ethanol to form a gel having no excess liquid. In molecular proportions this gives

| *Potassium ethyl sulphate.* | *Water.* | *Ethanol.* |
|---|---|---|
| 164 g. (1 mol.) | 109 g. (6 mols.) | 278 g. (6 mols.) |

On distillation, 164 g. of salt were recovered with 381 g. of mixed liquids, which, from specific gravity determinations, contained 110 g. of water and 271 g. of ethanol. A less volume of ethanol produces no gel and the colloid rapidly dissolves in excess. After about five minutes the gel exhibits syneresis and crystals gradually form in the liquid : these attain to a considerable size after twenty-four hours, if kept at 0°, but at 15° the gel persists for about forty-eight hours. On warming to 50° it rapidly dissolves and does not reform on cooling. It does not form the moment the precipitant is added, but only when a certain concentration of the alcohol is reached, which is when roughly four-fifths of the total dispersion medium is present. The intermicellar liquid cannot be withdrawn without destroying the colloid ; it is, therefore, a non-elastic gel. A thin film of the gel viewed under the microscope through a 1 inch objective within one minute of gel formation, shows a cloudy mass of minute dark points dispersed through it ; these rapidly form long, thin, colourless prisms, which do not redissolve, the whole finally becoming crystalline and the prisms gradually change to plates.

Acids, alkalis, glycerol, aniline and salts soluble in water, if added in small quantities, do not seem to inhibit the colloid formation, due possibly to the large quantity of solid present. But if they are added after the gel is formed, they cause more rapid deterioration of the colloid. No other single organic liquid was found to produce a gel, but many of them precipitated the salt in a crystalline condition. A fairly stiff, white opaque gel sets when made with 1 volume of a 166·26 per cent. aqueous solution of the salt with 4 volumes of a precipitant containing 1 volume of *n*-propyl alcohol and 5 volumes of ethanol. The ethyl sulphates of the other alkali and alkaline earth metals do not form aqueous gels by these methods, and, therefore, this salt might be used for the identification of either the ethyl sulphate or the potassium ions.

## Methanol Gels.

The methanol was purified by methods previously described,[1] and the purest obtainable sample of the salt was recrystallised twice from methanol solution, from which it came out at first in thin, needle prisms, which slowly changed to plates containing no alcohol of crystallisation[2]. After air drying for four hours and subsequent heating at 100° for thirty minutes, the solubility in methanol was determined as formerly described.[2] 2·18 g. of salt dissolve in 100 g. of methanol at 20°. The salt is insoluble in benzene, acetone, chloroform and most of the usual organic solvents except the lower, saturated, aliphatic alcohols ; nevertheless, few of them act as good dispersion media. Fairly solid, almost water-clear gels are produced from 1 volume of the above solution on the addition of 2 volumes

of tertiary amyl alcohol ; 2½ volumes of chloroform ; 5 volumes of methyl *n*-propyl carbinol ; clear but thinner ones with 2 volumes of benzene ; 2¼ volumes of *n*-butanol ; 4 volumes of hexyl alcohol or heptyl alcohol ; 5 volumes of β-methyl butanol ; 6 volumes of *n*-butanol ; 10 volumes of *n*-amyl alcohol ; 15 volumes of amyl acetate or *iso*-butyl acetate ; 20 volumes of methyl salicylate ; and thin opaque ones with 6 volumes of ether or *iso*-amyl alcohol and any volume of carbon tetrachloride. None form with ethanol, nitro-benzene, di-benzyl ether, bromobenzene, amyl nitrite, pyridine, pinene or the hydrocarbons of the camphor series, aliphatic hydrocarbons, carbon bisulphide, glacial acetic acid or aldehydes. With 40 volumes of aniline, if added slowly, a fairly solid opaque one will form but on rapid addition, crystals of the salt are at once thrown down. The aliphatic hydrocarbons form two layers. Fairly good gels may be made with some mixtures especially one with 3 volumes of an equivolume mixture of aniline and chloroform. Nearly all these gels are more easily formed if the salt solution is heated to about 50° and then about half of the cold precipitant added with agitation of the mixture ; when this agitation has ceased the second half is cautiously added and the whole allowed to stand for five minutes, otherwise crystal formation occurs. This phenomenon is the exact opposite of that, which was found in the formation of the sodium benzoate gels. These colloids vary in their permanency from ten seconds for that with methyl salicylate to three weeks or more for that with chloroform. Most of them exhibit syneresis more or less rapidly and dissolve in the exuded liquid, and finally deposit crystals of the salt. Many of them are easily destroyed by adding excess precipitant, and from such the intermicellar liquid cannot be withdrawn without a similar result occurring. These are non-elastic gels. The intermicellar liquids may with care be withdrawn from a few of them to just the opacity point, beyond which they rapidly deteriorate and they do not permit of the reabsorption of the same or any other liquid : these might be termed semi-elastic gels.

All these colloids may be formed in the absence of moisture, but all are very soluble in water. 100 g. of a gel, made with 1 volume of a 2·18 per cent. salt solution in methanol and 2½ volumes of chloroform, dissolves in 2·56 g. of water and in 7·91 g. of methanol at 20°. Viewed through the microscope, a thin film of the gel hanging from a cover glass showed the same phenomena, under the same conditions, as those found with the aqueous gel ; but if the cover glass is sealed to the slide with paraffin wax the colloid persists for at least twelve hours and subsequent crystal formation is very slow.

A few of the physical properties were examined.

**Heat** affects all these gels very rapidly after they are once formed. The most solid one, which is made with 2½ volumes of chloroform, on heating to 100°, rapidly boils and the colloid partially dissolves leaving broken portions in the liquid, but it does not reform on cooling.

**Low Temperature.**—A saturated salt solution in methanol at 20° deposited crystals at − 8°. A gel made with 1 volume of salt solution and 2½ volumes of chloroform did not freeze, but deposited crystals at − 15° and rapidly deteriorated : one made with 1 volume of salt solution and 3 volumes of tertiary amyl alcohol also did not freeze but began to deposit crystals at − 18° and persisted for more than an hour. It is, therefore, evident that these colloids exist only at or about average room temperature. This may be due to the small content of organic material in the molecule and also in the negative ion of the salt, inorganic material being, in general, more prone to crystallisation and less to colloid formation, over wide ranges of temperature, than is organic.

**Hydrogen and Hydroxyl Ionic Concentration** was found, for a gel made with chloroform, by using a universal indicator with precautions suggested by Michaelis and Mizutani.[3] A greenish yellow colour showed

[3] *Biochem. Z.*, **147**, 7, 1924.

a $p_H$ of a little over 7 ; this gel is, like those of calcium acetate and sodium benzoate, slightly alkaline.

**Electrical Conductivity** was taken at 20°, since, if the temperature was raised to the usual 25°, more rapid deterioration of the gel occurred. For methanol $K = 0.220 \times 10^{-5}$ and for the salt solution (2.18 g. of salt in 100 g. of methanol at 20°) $K = 0.3693 \times 10^{-3}$. For a gel made with 1 volume of salt solution and $2\frac{1}{2}$ volumes of chloroform, kept at 20° :

After 5 minutes from the addition of chloroform $K = 0.1051 \times 10^{-4}$
,, 30   ,,        ,,      ,,           ,,    $K = 0.0$
,, 2 hours ,,     ,,      ,,           ,,    $K = 0.6688 \times 10^{-5}$
,, 3   ,,    ,,      ,,      ,,           ,,    $K = 0.6026 \times 10^{-5}$
,, 4   ,,    ,,      ,,      ,,           ,,    $K = 0.5594 \times 10^{-5}$
,, 5   ,,    ,,      ,,      ,,           ,,    $K = 0.5853 \times 10^{-5}$
,, 18  ,,    ,,      ,,      ,,           ,,    $K = 0.6026 \times 10^{-5}$
,, 48  ,,    ,,      ,,      ,,           ,,    $K = 0.1404 \times 10^{-4}$
,, 7 days    ,,      ,,      ,,           ,,    $K = 0.1404 \times 10^{-4}$

These figures demonstrate that, although the outward appearance of the colloid suggests that it is a perfect gel, during the first half-hour it is only partly colloidal, and that a considerable quantity of the sol still remains, possibly as intermicellar liquid, which only slowly gelatinises : if this is the case, the radii of the capillaries at this stage may be much greater than after the lapse of that time. During the next one and a half hours syneresis and deterioration set in, but the latter is then arrested for about twenty-four hours and at the end of the next twenty-four hours, or even in seven days, the disintegration of the colloid is not complete. Since there is no question of setting on cooling, as with gelatine, the complete formation of the present gel is dependent on time and not on temperature, yet if the temperature be altered the time factor diminishes.

Any experiments on penetration or Liesegang rings were precluded by the ease with which the gels broke down, when any methanol soluble substance was added to them.

**Bubble Formation.**—If the salt solution is brought to the boil and chloroform added fairly rapidly, a clear, moderately solid gel containing bubbles is formed but it does not persist very long. These bubbles are almost spherical and little or no flattening was noticeable ; therefore, the internal pressure of the gel must be very small : in this it differs from those of calcium acetate and sodium benzoate.

**Optical Properties. Polarised Light.**—Though a chloroform gel seemed almost water clear in diffused daylight, a slight opalescence appeared in the polarimeter : this scattered the polarised light, which did not readily pass through it, thus making observation of the rotation somewhat difficult. Using a mercury vapour lamp the observed rotation was $- 2.2°$, when viewed through a tube 1 cm. diameter and 20 cm. long at 20°.

**Double Refraction.**—Faint irregular bands appeared between nicol prisms, but they were too indefinite for any colour changes to be seen on rotation, or to indicate any alteration under pressure.

**Refractive Indices.**—Only three of these gels were found to be suitable for this determination. Their observed refractive indices are shown in column 2 of the table and these agree with those of calcium acetate and

REFRACTIVE INDICES OF GELS MADE FROM SOLUTIONS OF POTASSIUM
ETHYL SULPHATE IN METHANOL AT 20°.

| Gels made with 1 Vol. of Salt Solution and | Refractive Indices of Gels. Found. | Refractive Indices of Sols. Calculated. | Differences. |
|---|---|---|---|
| $2\frac{1}{2}$ vols. of chloroform  .      . | 1.4149 | 1.4104 | 0.0045 |
| 2 vols. of $n$-butyl alcohol      . | 1.3746 | 1.3724 | 0.0022 |
| 2 vols. of tertiary amyl alcohol | 1.3956 | 1.3823 | 0.0133 |

sodium benzoate in being higher than those calculated for their respective sols.

Assuming that in $K$ the refraction of methanol and of potassium ethyl sulphate are additive, its value for the solution of 2·18 g. of salt in 100 g. of the alcohol was 0·364 calculated from the equation Lorenz [4] and Lorentz.[5]

$$K = \frac{1}{x}\left(\frac{\mu_s^2 - 1}{\mu_s^2 + 2} \times \frac{100}{d_s} - \frac{\mu_w^2 - 1}{\mu_w^2 + 2} \times \frac{100 - x}{d_w}\right),$$

where

*Values found.*

| | | |
|---|---|---|
| $K$ = the specific refraction of the salt in solution . . . | | — |
| $x$ = per cent of salt . . . . . . . | | 2·180 |
| $\mu_s$ = index of refraction of the solution at 20° . . | | 1·339 |
| $\mu_w$ = ,, ,, ,, ,, methanol at 20° . . | | 1·329 |
| $d_s$ = density of the solution at 20° . . . . | | 0·808 |
| $d_w$ = ,, methanol at 20° . . . . . | | 0·794 |

This value is between those found for sodium benzoate and calcium acetate, and it agrees with the position of the solubility of potassium ethyl sulphate, which lies similarly between those of the above two salts. If $S$, $M$, and $D$ represent the total volume of the sol, the volume of the methanol and the volume of the dispersion medium respectively, then the general expression for calculating $\mu_s$, the refractive indices of the sols, will be

$$K = \frac{1}{x}\left(\frac{\mu_s^2 - 1}{\mu_s^2 + 2} \times \frac{S}{d_s}\right) - \frac{1}{x}\left(\frac{\mu_w^2 - 1}{\mu_w^2 + 2} \times \frac{M}{d_w}\right) - \frac{1}{x}\left(\frac{\mu_z^2 - 1}{\mu_z^2 + 2} \times \frac{D}{d_z}\right)$$

where

$K$ = specific refraction of the salt in solution = 0·364 and $x$, $\mu_w$ and $d_w$ appear above.

Then at 20° for the sol with

| | Chloroform. | Iso-butanol. | Tertiary amyl alcohol. |
|---|---|---|---|
| $S =$ | 700 | 300 | 300 |
| $M =$ | 200 | 100 | 100 |
| $D =$ | 500 | 200 | 200 |
| $d_s =$ | 1·26 | 0·807 | 0·809 |
| $d_s =$ | 1·499 | 0·806 | 0·809 |
| $\mu_z =$ | 1·44 | 1·396 | 1·406 |

**Radii of the Capillaries.**—The ratio $p_s/p_w$, determined with Zsigmondy's apparatus [8] was introduced into the equation, used by Van Bemmelen [7] and Anderson,[8] from which the radii were calculated. The only one of these gels, from which the intermicellar liquid could be withdrawn whilst permitting the subsequent permanency of the colloid to remain sufficiently long for observations of $p_w$ to be made, was the one with 1 volume of salt solution and $2\frac{1}{2}$ volumes of chloroform.

From

$$r = \frac{2\sigma p d}{g m p_s p_r \log \dfrac{p_s}{p_w}}$$

[4] *Wied. Ann.*, 11, 70, 1880.          [5] *Ibid.*, 9, 642, 1880.
[6] *Z. anorg. Chemie*, 71, 356, 1911.    [7] *Ibid.*, 5, 466, 1894, *et seq.*
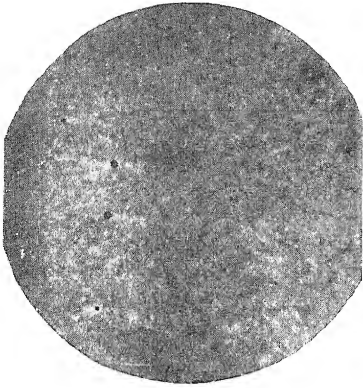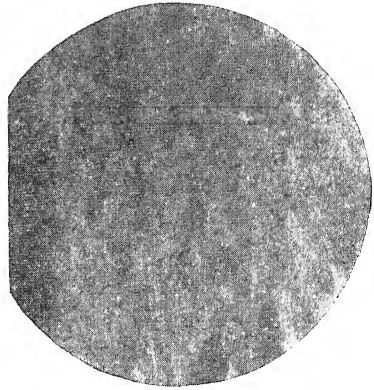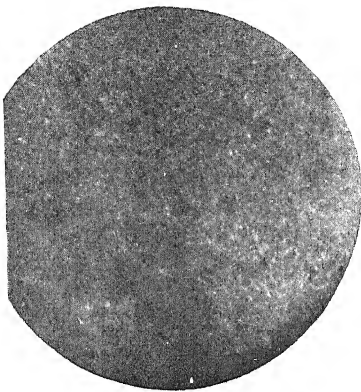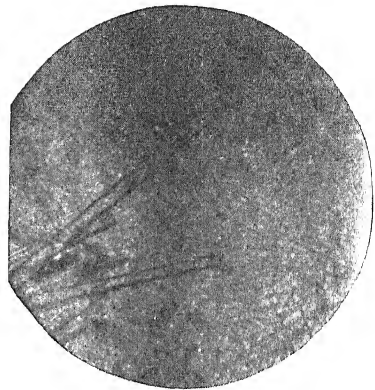[8] *Z. physik. Chemie*, 88, 191, 1914.

Fig. 1.



Fig. 2.



Fig. 3.



Fig. 4.

where

*Values found at* 15°

$r$ = capillary radius . . . . . —
$\sigma$ = surface tension of liquid mixture . . 20·69 dynes per cm.
$p_d$ = vapour density of mixture . . . 0·00281
$p_f$ = density of liquid mixture . . . 1·2883
$p_s$ = saturation pressure of gel at 15° . . 3·70
$p_w$ = vapour pressure of gel at opacity point . 2·60
$g$ = 981 dynes per cm. . . . . —
$m$ = density of mercury 13·5 . . . —

using a liquid mixture of 1 volume of methanol and 2½ volumes of chloroform, or 18 and 82 per cent. respectively by weight, the capillary radii came out to 5·34 × 10⁻⁷ cm.

The withdrawal of the intermicellar liquid presented some difficulty, since the opacity point is not very marked and if overstepped the colloid collapsed and prevented any observation of its vapour pressure. The small size of the capillaries may be due to the large quantity of inorganic material, of which the molecules of the salt are composed, which may cause the micellae to be of smaller size and so the whole may be closer packed than is the case where the organic content is larger.

**The Ultramicroscopic** view of thin films of the gel spread on cover glasses, through a $\frac{1}{12}$-inch oil-immersion lens, did not show up the micellae very well : they appeared to be very close together in strings, which had the appearance of crooked shining lines. Four stages of the decay of the gel are depicted in the photographs. No. 1. The lines of micellae. No. 2. The first indication of crystallisation (after an interval of about three hours). No. 3. After a further interval. No. 4. Crystals of the salt after the gel had dried (through a ½-inch objective). The larger crystals appeared to be rhombic holohedral prisms. No straight threads were seen in any of the films.

## Gels in other Solvents.

Potassium ethyl sulphate is soluble in some of the lower saturated aliphatic alcohols. Its solubility is 0·33 g. in 100 g. of ethanol at 20°. It will crystallise from a boiling solution on cooling. It forms a series of gels with some of the dispersion media used with the methanol solutions. They are very thin and soon disintegrate and deposit crystals. A fairly solid, but slightly opaque one, was formed by evaporating a boiling solution down to small bulk and cooling in an open vessel, without the addition of any precipitant. In propanol it dissolves to the extent of 0·15 g. and in *iso*-propanol 0·5 g. in 100 g. of solvent at 20°. Neither solution forms gels with liquid precipitants, but, like the solution in ethanol, does so on evaporation of the boiling solution. It is slightly soluble in warm glycerol, but forms no gel with it, and it is quite insoluble in the higher alcohols. Although the solubility of the salt in these three alcohols is so small, they do not act as precipitants for the methanol solution.

## Colloids with other Salts of Ethyl Sulphuric Acid.

In methanol solution at 15° the sodium salt gives a white, opaque gel with benzene, but none with any other dispersion media, which have so far been tried. The magnesium salt is not precipitated at all, and that of barium yields a colloidal precipitate only with aniline.

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# INERT GAS EFFECTS AT THE LOWER EX-PLOSION LIMIT OF PHOSPHINE-OXYGEN MIXTURES.

BY S. C. GRAY AND H. W. MELVILLE.

Recently a correlation between the kinetics of the stable chain oxidation and those of the explosion limits in phosphine-oxygen mixtures has been established.[1]  The data above and at the upper explosion limit have shown conclusively that, in this reaction at least, one of the carriers is an oxygen atom and that the principal cause of termination of reaction chains in the gas phase is due to the triple collision

$$O + O_2 + M \rightarrow O_3 + M,$$
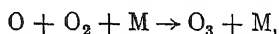
where M may be $O_2$, $PH_3$ or any inert gas present.

Furthermore, it would appear that nearly every such triple collision is effective in removing the oxygen atom.  This mode of termination of the chains becomes of importance when the pressure of oxygen is greater than 4 mm. and indeed gives rise to the appearance of the upper limit.

At lower pressures, however, the chains end upon the walls of the reaction tube with the result that inert gases, which function as inhibitors at higher pressures, now act as accelerators by the well-known process of impeding the diffusion of the reaction centres to the walls.  The quantitative theory of the effect has shown that the increase in chain length can be represented by the factor $(1 + \mu[X])/([PH_3] + [O_2])$ where $\mu$ is a constant dependent on the nature of the inert gas but independent of its pressure.  The early results,[2] however, exhibit a distinct decrease in the value of $\mu$ as the pressure of the inert gas increases.  Table I. shows some typical figures :—

TABLE I.

| Nitrogen (Series D). | | | | Argon (Series E.) | | | |
|---|---|---|---|---|---|---|---|
| $[O_2]$. mm. | $[PH_3]$. mm. | $[N_2]$. mm. | $\mu$. | $[O_2]$. | $[PH_3]$. | $[A]$. | $\mu$. |
| 0·85 | 0·61 | — | | . 1·05 | 0·70 | — | — |
| 0·82 | 0·59 | 0·54 | 1·82 | 0·84 | 0·56 | 0·51 | 1·54 |
| 0·68 | 0·49 | 1·68 | 0·39 | 0·70 | 0·51 | 1·11 | 1·03 |
| 0·64 | 0·46 | 3·24 | 0·26 | 0·69 | 0·46 | 1·59 | 0·96 |
| | | | | 0·65 | 0·44 | 2·09 | 0·82 |
| | | | | 0·67 | 0·45 | 2·86 | 0·63 |

This falling off in the magnitude of $\mu$ was attributed to gas phase inhibition without specifying its nature.  From the data obtained at the upper limit, it is easy to show that gas phase inhibition should be

[1] Melville and Roxburgh, *J. Chem. Physics,* **2,** 739, 1934.  Previous references to the kinetics of the reaction are given in this paper.

[2] Dalton and Hinshelwood, *Proc. Roy. Soc.,* **125A,** 294, 1929.

entirely negligible at the pressures employed at the lower limit. Using the same notation as before, the chain length with wall and gas termination is respectively given by

$$\nu_{\text{wall}} = k[\text{PH}_3][\text{O}_2]/K \cdot \{1 + \mu[\text{X}]/([\text{PH}_3] + [\text{O}_2]\} \, . \qquad . \quad (1)$$

$$\nu_{\text{gas}} = \frac{k[\text{PH}_3]}{k_6[\text{O}_2]([\text{O}_2] + [\text{X}])} \cdot \quad . \quad . \quad . \quad . \quad (2)$$

where $k$ is the velocity coefficient for the propagation reaction; $K$ is the rate at which O atoms diffuse to the walls at a total pressure of 1 mm., $k_6$ is the velocity coefficient for the removal of O atoms in the ternary collision. From the position of the minimum in the explosion curve, which is at 4·62 mm. $\text{O}_2$ for a 2 cm. tube, it can be shown [1] that $\sqrt[3]{K/2k_6} = 4\cdot62$. In one experiment [2] in Series D (nitrogen) the value of $\mu$ fell to 0·26 when $[\text{PH}_3] = 0\cdot46$, $[\text{O}_2] = 0\cdot64$, $[\text{N}_2] = 3\cdot24$. The ratio gas to wall deactivation is given by

$$\frac{1/\nu_{\text{gas}}}{1/\nu_{\text{wall}}} = [\text{O}_2]/K\{1 + \mu[\text{X}]/([\text{PH}_3] + [\text{O}_2]\}k_6[\text{O}_2]([\text{O}_2] + [\text{X}] \, . \quad (3)$$

Taking $\mu = 0\cdot71$ (*vide infra*), and substituting the above values, this ratio is 0·025, so that at these pressures only 1/40 of the chains terminate in the gas phase.

Apart from this discrepancy, the remainder of the observations on the behaviour of the reaction appeared to be in so good agreement with theory as to warrant a repetition and extension of the earlier results on the effect of inert gases at the lower limit to make sure that there was no additional kind of gas phase deactivation to be included in the theoretical treatment.

### Experimental.

Two methods were employed in determining the position of the lower limit. The first consisted in measuring the gases into the reaction vessel, compressing the mixture until it exploded, and from the original pressure and known volume change, calculating the pressure at the explosion point. In the second, the inert gas and phosphine were passed into the reaction tube, and oxygen allowed to enter slowly through a capillary until explosion took place. Of these methods the second proved much superior, since it yielded more consistent results.

The principal part of the apparatus is shown in Fig. 1. Exhaustion was effected by a mercury condensation pump backed by an oil pump. Phosphine was stored in B



FIG. 1.

and the various inert gases and organic liquids in separate reservoirs. Oxygen entered by the capillary at the end of which there was a two-
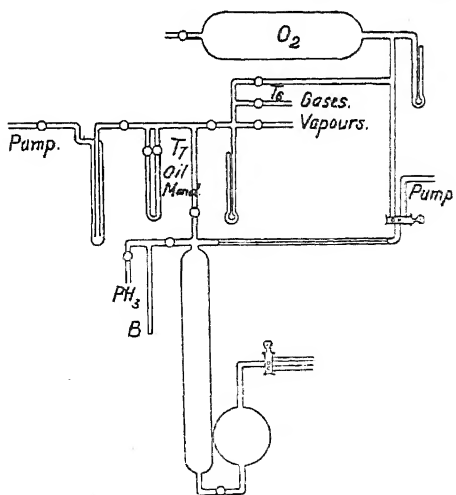
way tap for arresting the flow after the explosion. The procedure was (a) to raise and lower the mercury to wash the walls with phosphoric acid, (b) admit phosphine from B, its pressure being recorded on the oil manometer, (c) admit the inert gas by opening $T_6$. After a short interval to allow the gases to mix, $T_7$ was closed to avoid slight solution of the gases in the oil and oxygen admitted until there was explosion, the time of entry being noted by stop watch. The explosion pressure was then calculated by means of previous calibration experiments. The walls were again washed preparatory to carrying out the next explosion.

The following gases and vapours were employed : $H_2$, Ne, A, $N_2$, $CO_2$, $N_2O$, $SO_2$, $PbMe_4$, $CCl_4$, $C_6H_6$, $C_2H_4$.

The gases were prepared as described in previous papers. The neon contained 2 per cent. helium and the condensable gases were fractionated with liquid air as were the liquids. The benzene and carbon tetrachloride were free from sulphur. The lead tetramethyl was prepared in the following way.

Twenty-four gm. magnesium foil, dried in a steam oven were placed in a 1-litre flask, and covered with 400 c.c. absolute ether, dried over sodium and redistilled. A reflux condenser fitted with a calcium chloride tube was attached and 142 gm. methyl iodide added in small quantities through the condenser. The flask was removed from the water bath and 125 gm. lead chloride added in small portions through the condenser. The mixture was heated for a few minutes, cooled to 0° C. and the magnesium compound decomposed by the addition of 200 c.c. water, the mixture being finally heated to complete the reaction. The contents of the flask were filtered through cotton wool into a separating funnel and the aqueous layer run off. The ethereal layer was dried over calcium chloride and the ether removed. The residue was transferred to a small distilling flask and re-distilled several times, the fraction passing over at 108-110° being collected. Distillation was continued until no residue was left in the distilling flask. Yield of purified product 30-40 gram.

## Discussion of Results.

It has been mentioned previously that the acceleration brought about by inert gases is given by the factor $1 + \mu[X]/([PH_3 + O_2])$. The calculation of $\mu$ is thus dependent on the accuracy with which this relationship holds, two simplifying assumptions being made in its deduction, namely that the two carriers $X_O$ and $X_P$ react equally readily with phosphine and oxygen respectively, and are destroyed on impact with the walls at similar velocities. This naturally gives rise to the symmetrical formula for the explosion limit $[PH_3][O_2]$ = const. If, however, $X_O$ reacts more rapidly with $PH_3$ than $X_P$ with $O_2$, then it can be shown that the explosion limit is given by $[O_2]\{[PH_3] + [O_2]\}$ = const., whereas if $X_P$ reacts
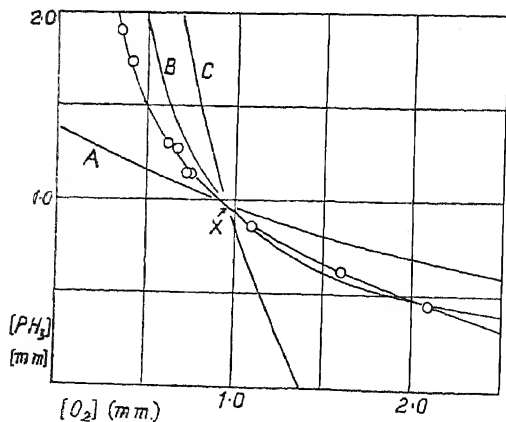


FIG. 2.

more quickly $[PH_3]\{[PH_3] + [O_2]\}$ = const.   A series of typical results has therefore been plotted in Fig. 2.   Three curves have been drawn through the point X, the intersection of the line drawn at 45° to the $[O_2]$ axis and the explosion curve, *viz.*,

$$(A) \ldots [O_2]\{[PH_3] + [O_2]\} = 1\cdot80 ;$$
$$(B) \ldots [PH_3][O_2] = 0\cdot90 ;$$
$$(C) \ldots [PH_3]\{[PH_3] + [O_2]\} = 1\cdot80,$$

from which it will be seen that the symmetrical equation conforms most closely with experiment.

Some typical results are given in Tables II. and III.   In the last column $[PH_3][O_2]\{1 + [X]/[PH_3] + [O_2]\}$ has been calculated to demonstrate that this product remains constant up to high inert gas pressures and also to indicate the consistency in the explosion pressures.   Such consistency could not be attained in the compression method.   The series of experiments,

TABLE II.

| $[PH_3]$. | $[O_2]$. | $[X]$. |
|---|---|---|
| **Inert Gas Hydrogen.** | | |
| 0·66 | 1·36 | — |
| 0·65 | 1·38 | 0·23 |
| 0·65 | 1·39 | 0·65 |
| 0·66 | 1·36 | 1·10 |
| 0·66 | 1·38 | 1·42 |
| 0·65 | 1·34 | 0·86 |
| 0·64 | 1·41 | — |

TABLE III.

| $[PH_3]$. | $[O_2]$. | $[X]$. | $[PH_3][O_2]\left\{1+\dfrac{[X]}{[PH_3]+[O_2]}\right\}$. | $[PH_3]$. | $[O_2]$. | $[X]$. | $[PH_3][O]_2\left\{1+\dfrac{[X]}{[PH_3]+[O_2]}\right\}$. |
|---|---|---|---|---|---|---|---|
| **Inert Gas SO$_2$.** | | | | **Inert Gas CO$_2$.** | | | |
| 0·64 | 1·05 | 0·22 | 0·76 | 0·66 | 1·38 | — | — |
| 0·59 | 0·78 | 0·63 | 0·68 | 0·71 | 1·18 | 0·22 | 0·94 |
| 0·55 | 0·55 | 1·06 | 0·60 | 0·62 | 1·14 | 0·43 | 0·88 |
| 0·40 | 0·54 | 1·52 | 0·78 | 0·59 | 0·95 | 0·88 | 0·83 |
| 0·43 | 0·61 | 1·29 | 0·58 | 0·59 | 0·87 | 1·08 | 0·90 |
| 0·53 | 0·75 | 0·86 | — | 0·56 | 0·81 | 1·26 | 0·89 |
| 0·64 | 1·34 | — | — | 0·54 | 0·77 | 1·52 | 0·91 |
| | | | | 0·45 | 0·71 | 1·95 | 0·88 |
| | | | | 0·43 | 0·57 | 2·63 | 0·88 |
| | | | | 0·32 | 0·61 | 3·23 | 0·88 |
| **Inert Gas N$_2$O.** | | | | **Inert Gas Nitrogen.** | | | |
| 0·64 | 1·34 | — | — | 0·64 | 1·38 | — | — |
| 0·64 | 1·20 | 0·44 | 0·95 | 0·65 | 1·15 | 0·43 | 1·02 |
| 0·62 | 1·07 | 0·65 | 0·91 | 0·62 | 1·12 | 0·68 | 0·97 |
| 0·58 | 1·00 | 0·88 | 0·91 | 0·58 | 1·02 | 1·08 | 1·00 |
| 0·55 | 0·99 | 1·08 | 0·93 | 0·58 | 0·96 | 1·29 | 1·03 |
| 0·53 | 0·92 | 1·30 | 0·93 | 0·57 | 0·83 | 1·73 | 1·05 |
| 0·49 | 0·90 | 1·54 | 0·94 | 0·51 | 0·74 | 2·36 | 1·09 |
| 0·31 | 0·87 | 2·77 | 0·90 | 0·43 | 0·73 | 3·03 | 1·12 |
| 0·39 | 0·79 | 2·28 | 0·91 | | | | |
| **Inert Gas Neon.** | | | | **Inert Gas Argon.** | | | |
| 0·66 | 1·41 | — | — | 0·60 | 1·48 | — | — |
| 0·63 | 1·34 | 0·23 | 0·95 | 0·63 | 1·19 | 0·45 | 0·94 |
| 0·61 | 1·26 | 0·69 | 0·94 | 0·63 | 1·10 | 0·64 | 0·95 |
| 0·57 | 1·21 | 1·07 | 1·10 | 0·60 | 1·07 | 0·86 | 0·98 |
| 0·52 | 1·12 | 1·52 | 1·11 | 0·58 | 1·05 | 1·07 | 1·01 |
| 0·57 | 1·26 | 0·88 | 1·07 | 0·57 | 0·96 | 1·30 | 1·02 |
| | | | | 0·56 | 0·90 | 1·56 | 1·03 |

carried out at different stages in the investigation, show the degree of concordance among the runs :

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Nitrogen . | . | $\mu = 0.72$ | 0.73 | 0.68 | 0.72 | 0.69 | 0.73 | 0.70 |
| Neon | . | $\mu = 0.52$ | 0.52 | 0.51 | 0.55 | 0.52 | 0.55 | 0.52 |

The value of the inert gas coefficient $\mu$ for each gas is given in Table IV., each being the mean of several runs. The quantity $1/[PH_3][O_2]$ has been plotte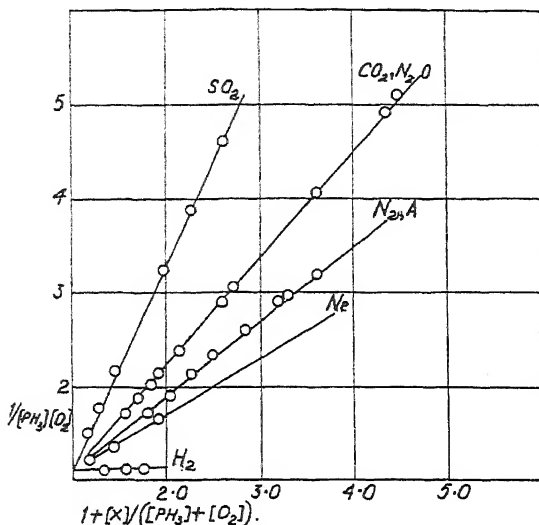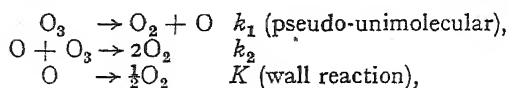d against $1 + [X]/([PH_3] + [O_2])$ in Fig. 3. It will be observed that there is no tendency for the lines to curve round at the highest inert gas pressures used in these experiments, although if much higher pressures had been employed such a curvature would be observed having its origin in the type of collision responsible for the existence of the upper limit. The effect of sulphur dioxide is somewhat greater than that anticipated on the diffusion theory, and consequently great care was taken in



FIG. 3.

its fractionation, but repetition of the experiments yielded exactly the same value of $\mu$.

Shortly after the diffusion effect was noticed, a table of inert gas coefficients was compiled from the results then available.[3] This table can now be considerably extended to demonstrate how nearly all the results fit in with theoretical expectations. Taking the hydrogen-oxygen first, it will be seen that the $\mu$'s from the thermal and spark lower limit agree fairly well, and, moreover, occupy their expected place in the horizontal column of the table in that $\mu$ decreases from $H_2 - O_2$ to $P_4 - O_2$. The values obtained above the upper limit from the stable reaction appear to be somewhat high, which would suggest that, in addition to impeding diffusion, these gases may play some part in facilitating initiation of chains.

Of considerable interest is the comparison between the oxidation of phosphine and the thermal decomposition of ozone. First it is necessary to explain how $\mu$ is determined for ozone, since the calculation is not so straightforward as in the case with the other reactions.

Under suitable conditions [6] ozone decomposes according to the following scheme :—

$$O_3 \rightarrow O_2 + O \quad k_1 \text{ (pseudo-unimolecular)},$$
$$O + O_3 \rightarrow 2O_2 \quad k_2$$
$$O \rightarrow \tfrac{1}{2}O_2 \quad K \text{ (wall reaction)},$$

[3] Melville, *Trans. Faraday Soc.*, **28**, 814, 1932.

TABLE IV.—Reaction and Origin of Results.

| Inert Gas. | $H_2 - O_2$,[4] Lower Limit Thermal. | $H_2 - O_2$, Lower Limit Spark. | $H_2 - O_2$, Above Upper Limit. | $CH_4 - O_2$, Lower Limit Spark. |
|---|---|---|---|---|
| $H_2$ . . | — | — | — | — |
| He . . | 0·30 | 0·15 | 2·3 | — |
| Ne . . | — | — | — | — |
| $N_2$ . . | 1·10 | 2·35 | 5·1 | 1·2 |
| A . . | 0·9 | 1·16 | 7·3 | 0·8 |
| $O_2$ . . | — | — | — | — |
| $CO_2$ . . | 0·39 | 2·4 | — | 1·5 |
| $N_2O$ . . | — | 4·8 | — | — |
| $SO_2$ . . | — | 2·6 | — | 2·7 |
| $CCl_4$ . . | — | 5·6 | — | 3·4 |
| $CHCl_3$ . . | — | 6·9 | — | 3·0 |

TABLE IV. (*continued*).

| Inert Gas. | $PH_3 - O_2$,[5] Lower Limit. | $O_3$,[6] Thermal Decomp. | $H_2S - O_2$, Lower Limit, Filament. | $CS_2 - O_2$, Lower Limit, Filament. | $CO - O_2$,[7] Lower Limit, Thermal. | $H_2 - Br_2$,[8] Photo Synthesis. | $P_4 - O_2$, Lower Limit. |
|---|---|---|---|---|---|---|---|
| $H_2$ . | <0·1 | 0·21 * | — | — | — | 0·09 | 0·10 |
| He . | — | 0·23 | — | — | — | 0·20 | 0·13 |
| Ne . | 0·52 | 0·47 * | — | — | — | — | 0·20 |
| $N_2$ . | 0·71 | 0·73 | 0·44 | 0·42 | 0·6 | 1·03 | 0·37 |
| A . | 0·77 | 0·83 | 0·59 | 0·64 | 1·2 | — | 0·46 |
| $O_2$ . | — | 0·71 | — | — | — | 1·03 | — |
| $CO_2$ . | 1·04 | 0·82 * | — | 0·83 | — | 1·25 | 0·48 |
| $N_2O$ . | 1·04 | 0·82 * | — | — | — | — | 0·46 |
| $SO_2$ . | — | 0·96 * | — | 0·92 | — | — | 0·52 |
| $CCl_4$ . | — | 1·72 * | — | — | — | 4·30 | 0·84 |
| $CHCl_3$ . | — | — | — | — | — | — | 0·84 |

* Calculated.

which yields

$$-\frac{d[O_3]}{dt} = k_1[O_3]\left\{1 + \frac{k_2[O_3]}{k_2[O_3] + K}\right\} \qquad . \qquad . \quad (4)$$

$k_1$, $k_2$ and $K$ are velocity coefficients. $K$ is proportional to $(1/D_{O_3} + 1/D_X)^{-1}$ where $D_{O_3}$ and $D_X$ represent the diffusion coefficients of O atoms through ozone and the inert gas respectively. $\mu$ is defined by the equation

$$R_X/R_0 = 1 + \mu[X]/[O_3] \quad . \qquad . \qquad . \quad (5)$$

where $R_X/R_0$ is the relative increase in velocity of that process which is affected by wall deactivation when inert gas is added. But

$$R_X/R_0 = \frac{K(\text{in absence of X})}{K(\text{in presence of X})} = \frac{1/D_{O_3} + 1/D_X}{1/D_{O_3}} = 1 + D_{O_3}/D_{O_2} \quad (6)$$

therefore from the observed increase in the rate of ozone decomposition and the above kinetic equation, the two values of $K$ may be readily

[4] Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.*, **138A**, 311, 1932.
[5] Present investigation.
[6] M. Ritchie, *Proc. Roy. Soc.*, **146A**, 848, 1934.
[7] Hadman, Thompson and Hinshelwood, *Proc. Roy. Soc.*, **138A**, 297, 1932.
[8] M. Ritchie, *Proc. Roy. Soc.*, **146A**, 828, 1934.

calculated. Since $D_{O_3} = \dfrac{\text{const.}}{\sigma_{O - O_3}^2}(1M/_O + 1/M_{O_3})^{\frac{1}{2}}[O_3]^{-1}$, where $\sigma_{O - O_3}$ is the sum of the radii of O and $O_3$, then $\mu$ is given by

$$\mu = \frac{1/\sigma_{O - O_3}^2(1/M_O + 1/M_{O_3})^{\frac{1}{2}}}{1/\sigma_{O - X}^2(1/M_O + 1M_X)^{\frac{1}{2}}} \qquad . \qquad . \qquad . \quad (7)$$

The value of $\mu$ thus computed is in excellent agreement with experiment, and justifies the calculation of $\mu$ for other gases, although these have not yet been measured.

The concordance in the values of $\mu$ for the phosphine and ozone re-actions is so close that it provides further reliable evidence that the oxygen atom is one of the carriers in the former reaction. The carbon monoxide results are subject to some uncertainty for the explosion curve is not represented accurately by a rectangular hyperbola. One important point may be mentioned about the $H_2 - Br_2$ results, and it applies in a modified degree to the $H_2 - O_2$ reaction. In the rigorous theory of the diffusion effect, account should be taken of the fact that the carriers do not diffuse through the reactants at the same speeds—the diffusion coefficient of bromine atoms through hydrogen is 8·4 times greater than that through bromine vapour at the same pressure. The value of $\mu$ will consequently be dependent on the composition of the mixture, increasing with the percentage of hydrogen. This is the reason for $\mu$ being so large in the $H_2—Br_2$ reaction, since $[H_2] = 200$, $[Br_2] = 15$ and $[HBr] = 4·5$. If equimolecular mixtures had been employed, the value of $\mu$ would have been much smaller, thus falling into line with the other reactions given in the table.

## Inhibition at the Lower Limit.

In marked contrast to the behaviour of the simple inert gases, ethylene, benzene, carbon tetrachloride, and lead tetramethyl raise the lower limit when added in relatively small quantities (Table V.). Moreover, it is noteworthy that these molecules all lower the explosion limit of $P_4 - O_2$ mixtures. At first, it would appear that a strange anomaly exists between the two reactions, in other respects so exactly similar, but a simple explanation is obvious when the problem is treated in the following way. It will be assumed that inhibition at these low pressures is due to the removal of oxygen atoms, $X_O$, by the foreign gas or vapour and that the rate of the reaction is $k'[X_O][X]$. The stationary concentration of $X_O$ is thus reduced, and the expression for $[X_O]$ becomes

$$\frac{d[X_O]}{dt} = I + k[X_P][O_2] - k[X_O][PH_3] - K[X_O] - k'[X_O][X] = 0 \quad (8)$$

I being the rate at which $X_O$ is produced spontaneously in the explosive reaction and photochemically in the stable reaction. $[X_P]$ is not affected, therefore

$$\frac{d[X_P]}{dt} = k[X_O][PH_3] - k[X_P][O_2] - K[X_P] = 0 \qquad . \quad (9)$$

On solving these equations and simplifying on the assumption that the chains are long.

$$-\frac{d[PH_3]}{dt} = \frac{Ik[PH_3]/K'}{1 + k'[X]/K' + [PH_3]/[O_2]} \qquad . \qquad . \quad (10)$$

TABLE V.

| Foreign Gas. | [PH₃]. | [O₂]. | [X]. | k'/k. |
|---|---|---|---|---|
| CCl₄ . . . | 0·67 | 1·41 | — | — |
| | 0·65 | 2·71 | 0·20 | $1 \cdot 5 \times 10^{-3}$ |
| | 0·66 | 1·40 | — | — . |
| PbMe₄ . . . | 1·28 | 0·89 | — | — . |
| | 1·29 | 1·59 | 0·11 | $5 \times 10^{-3}$ |
| | 1·48 | 2·00 | 0·22 | $3 \cdot 6 \times 10^{-3}$ |
| | 1·77 | 2·62 | 0·32 | $3 \cdot 1 \times 10^{-3}$ |
| C₆H₆ . . . | 1·27 | 0·87 | — | — |
| | 1·30 | 1·07 | 0·11 | $2 \cdot 4 \times 10^{-3}$ |
| | 1·29 | 0·86 | — | — |
| | 1·30 | 1·04 | 0·09 | $2 \cdot 3 \times 10^{-3}$ |
| | 1·32 | 2·21 | 0·32 | $2 \cdot 5 \times 10^{-3}$ |
| | 1·33 | 1·38 | 0·21 | $2 \cdot 3 \times 10^{-3}$ |
| C₂H₄ . . . | 0·65 | 1·44 | — | — |
| | 0·64 | 1·70 | 0·106 | $0 \cdot 8 \times 10^{-3}$ |
| | 0·65 | 1·82 | 0·125 | $1 \cdot 0 \times 10^{-3}$ |

Direct photo-oxidation, Zn spark.*

| C₂H₄. | [PH₃]. | [O₂]. | [C₂H₄]. | $t_{\frac{1}{4}}$. | k'/k. |
|---|---|---|---|---|---|
| | 0·461 | 0·866 | — | 27 | — |
| | 0·480 | 0·918 | 0·605 | 82 | $0 \cdot 9 \times 10^{-3}$ |
| | 0·271 | 0·502 | — | 46 | — |
| | 0·269 | 0·504 | 0·466 | 80 | $0 \cdot 7 \times 10^{-3}$ |

$t_{\frac{1}{4}}$ is the time in seconds for the reaction to go 25 per cent. to completion.

* The authors are indebted to Dr. H. L. Roxburgh for these data.

If $R_0$ and $R$ be the rates in absence of and in presence of X, then

$$R_0/R_X = 1 + \frac{k'}{K}[X][O_2]\left(1 + \frac{\mu[X]}{[PH_3] + [O_2]}\right) . \qquad . \quad (11)$$

where $K$ is the value of $K'$ at a total pressure of 1 mm. of $PH_3$ and $O_2$, $\mu$ is the inert gas coefficient for X. On substituting the appropriate values $k'/k$ may be calculated. But $\nu$, the chain length below the lower limit is given by $\nu = k/K[PH_3][O_2]$, $k/K$ and $k'/k$ may therefore be computed. If it is further assumed that the propagation collisions are 100 per cent. efficient, then the ratio $k'/k$ gives the efficiency of the inhibition collisions directly.

In the explosive reaction account must be taken of branching and the equation for $[X_0]$ becomes

$$\frac{d[X_0]}{dt} = I + \alpha k[X_P][O_2] - k[X_0][PH_3] - K[X_0] - k'[X_0][X] = 0 \quad (12)$$

$(\alpha - 1)$ being the probability of branching. On solving these equations, equating the coefficients of terms containing $[X_0]$ to zero and carrying out the necessary simplifications, the explosion pressures are given by the equation

$$[O_2](k(\alpha - 1)[PH_3] - k'[X]) = K(1 + \mu[X]/([PH_3] + [O_2]) \quad . \quad (13)$$

It can now be seen why the oxidation of phosphine is much more sensitive to poisons than is the oxidation of phosphorus. Although the magnitude of the propagation coefficients are probably similar, the probability of

branching is widely different.   For $P_4 - O_2$ ($\alpha - 1$) is about $10^{-1}$, and [1]
for $PH_3 - O_2$, $10^{-3}$.   If $X_O$ in the phosphorus reaction is also an oxygen
atom and therefore similar inhibitive processes are at work in the two
reactions, then the phosphine reaction will be 100 times more sensitive
to a given poison.   It is therefore not surprising that benzene, ethylene,
carbon tetrachloride behave as inert gases in the $P_4 - O_2$ reaction by
lowering the limit, whereas they act as strong poisons in the $PH_3 - O_2$
reaction by raising the limit.   By substituting the figures in Table III.
in equation (13), the ratio $k'/k$ has been evaluated for each gas, and is
given in the last column of the table.   The required values of $\mu$ were
calculated by analogy with the other reactions listed in Table II.   $k'/k$
obtained for ethylene from the explosive data may be checked by measur-
ing the retardation of the stable photochemically induced oxidation below
the lower limit.   Ethylene does not absorb the radiation of the zinc
spark which is responsible for the dissociation of phosphine and thus
no correction on this account need be applied.   Again, it is a marked
inhibitor although acceleration by inert gases (e.g., argon) is also dis-
played in the same pressure range.[9]   Employing equation (11), $k/K$
has been evaluated, and as $\nu$ in the tube used was 800 for 0·50 mm. $PH_3$
and 0·50 mm. $O_2$, $k/K = 3200$, $k'/k$ is given in the last column.   The
agreement between the values is exceedingly good considering the
different nature of the two reactions.   Relatively the stable reaction is
less sensitive to poisons because the chain length is shorter than that at
the explosion limit, the determination of $k'$ is thus more accurate.   This
method is, of course, limited by the fact that most of the inhibitors
absorb light of longer wave-length than phosphine itself.

The relative, and on certain suppositions the absolute, values of the
inhibition coefficients for the $P_4 - O_2$ reaction can be obtained from their
influence on the upper limit.[10]   If the two reactions are really identical in
that $X_O$ is an oxygen atom, it would be expected that at least the relative
values of $k'$ would be identical.   Such is apparently not the case.   For
$P_4 - O_2$, benzene and sulphur dioxide are both weak inhibitors, whereas
for $PH_3 - O_2$, the latter behaves as an inert gas and the former as an
inhibitor.   Similarly, ethylene is ten times more powerful than benzene
in $P_4 - O_2$, but exerts about the same effect on $PH_3 - O_2$.   Lead
tetramethyl is a comparatively weak inhibitor for $PH_3 - O_2$, contrasting
with the powerful inhibitive action of lead tetraethyl [10] in $P_4 - O_2$.
There are, unfortunately, no data at the upper limit of $PH_3 - O_2$
mixtures to check the magnitude of the inhibition observed at the lower
limit.

## Summary.

The effect of foreign gases on the lower explosion limit of $PH_3 - O_2$
mixtures has been determined as accurately as the experimental conditions
will permit.   $H_2$, Ne, A, $N_2$, $CO_2$, $N_2O$, and $SO_2$ all lower the limit in the
normal way by impeding the diffusion of the chains to the walls.   There is

[9] Melville, *Proc. Roy. Soc.*, **138**A, 389, 1932.
[10] Melville, *Trans. Faraday Soc.*, **28**, 312, 1932.

no measurable gas phase inhibition when the pressure of the gas is of the same order as that of the phosphine and oxygen. This agrees with observations on the effect of some of these gases on the upper limit.

$C_2H_4$, $C_6H_6$, $PbMe_4$, and $CCl_4$ all raise the lower limit in marked contrast to the lowering of the limit observed with $P_4 - O_2$ mixtures. It is shown that the reason for the difference is that the probability of branching of chains in the $PH_3 - O_2$ reaction is less than that in $P_4 - O_2$ mixtures, and that a given inhibitor exerts a more powerful influence on the former reaction. The value of the inhibition coefficient has been calculated and in the case of ethylene, checked by measuring the inhibition of the stable photo oxidation of phosphine.

An extended table of inert gas coefficients has been compiled.

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# THE OXIDATION OF CARBON MONOXIDE BY NITROUS OXIDE.

## By C. E. H. Bawn.

During the last few years many reactions have been discovered which display the phenomena of explosion limits. The reaction between carbon monoxide and oxygen is of this type.[1] In quartz vessels and in the neighbourhood of 600° C. and within certain limits of pressure these gases combine explosively whilst outside of this region a slow but measureable reaction occurs. The existence of these limiting pressures defining a region of explosive combination can be satisfactorily explained by the theory of branching chains.[2] However, on account of the variable nature of the slow reaction and the occurrence of metastability phenomena [1] it has neither been possible to provide a clear mechanism of the chemical changes involved in the carbon monoxide-oxygen chain nor to determine the condition under which the slow reaction gives rise to explosion at the lower limit. Furthermore, the remarkable influence of added carbon dioxide on the reaction [3] appears to provide a new problem in energy transfer. In order to obtain further information on these facts it seemed of interest to study the oxidation of carbon monoxide using nitrous oxide as the oxidising agent, since it is known that this simulates the direct oxidation in many respects, and that both are catalysed in a remarkable manner by water vapour. Also preliminary investigation showed that at temperatures at which rapid reaction occurred, the unimolecular decomposition of nitrous oxide has commenced. It seemed hopeful, therefore, that some information might be obtained concerning the part played by oxygen atoms in the reaction. The investigations fall naturally into two separate studies (1) the measurable reaction and (2) the explosive oxidation, and will be considered in that order.

[1] Hadman, Thompson and Hinshelwood, *Proc. Roy. Soc.*, **138A,** 297, 1932, where other references are given.
   [2] Semenoff, *Z. Physik,* **46,** 109, 1927 ; **48,** 571, 1928.
   [3] Garner and Cosslett, *Trans. Faraday Soc.*, **27,** 176, 1931.

## Experimental.

The apparatus used is shown in Fig. 1. The reaction vessel was heated in an electric furnace A (35 cm. long and 5 cm. diam.) enclosed in a large iron box (35 cm. by 28 cm.) which was packed with insulating material. The temperature was measured with a platinum-rhodium thermocouple which had been calibrated : it was constant to within 1° over the central part
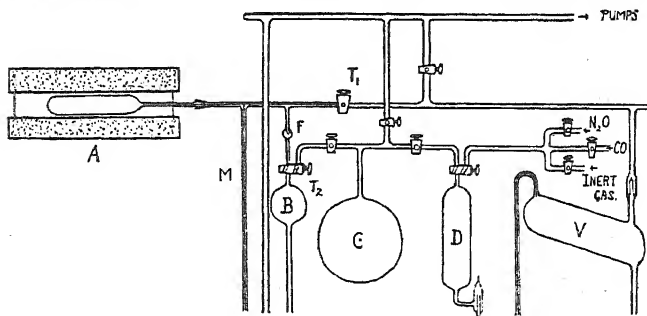


FIG. 1.

of the furnace (20 cm.). The pressure in the system was measured by the capillary manometer using a cathetometer. The reaction vessels had the following dimensions : A vol. 148·2 c.c. diam. 3·7 cm. ; B vol. 123·7 c.c. diam. 3·7 cm. ; C was the same as B but was packed with pieces of quartz tube. The total volume external to the furnace was not greater than 7 c.c.

## Preparation of Gases.

**Nitrous Oxide** was obtained from a cylinder. The gas which was already more than 99 per cent. $N_2O$ was further purified by passage through ferrous sulphate (to remove nitric oxide), caustic potash, and condensed out in a vessel cooled in liquid air. Any nitrogen was then removed by evacuation, the liquid air replaced by solid carbon dioxide and alcohol, and the gas collected which evaporated between − 80° and − 40° C. The gas was finally dried by leaving it in contact with fresh phosphoric oxide.

**Carbon Monoxide** was prepared by dropping formic acid on to conc. sulphuric acid and purified by passage through caustic potash and dried as before.

**Carbon Dioxide** was prepared by the action of hydrochloric acid on marble chips ; it was washed by passage through water containing suspended silver oxide. The gas was condensed in liquid air, any permanent gases being removed by evacuation and finally allowed to vaporise from a vessel cooled to − 50° C. It was stored in a large gasholder in contact with phosphoric oxide.

**Nitric Oxide** was obtained from ferrous sulphate, sodium nitrite and hydrochloric acid precisely as described by Moser (*Die Reindarstellung von Gasen*, page 87). It was purified by fractional distillation.

**Inert Gases** were obtained from cylinders. These gases were allowed to stand over water for a considerable period and finally passed over charcoal (which had been previously baked out in vacuo at 300° C.) cooled to liquid air temperature (solid carbon dioxide and alcohol in the case of argon). The gases were dried as before.

**Procedure.**—Since the reaction occurs without change of pressure

$$N_2O + CO \rightarrow CO_2 + N_2 \qquad . \qquad . \qquad . \quad (1)$$
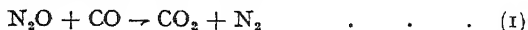
manometric methods could not be used and the rate was followed by direct estimation of the carbon dioxide formed. The usual method of carrying

out an experiment was to admit a known volume of the gas mixture from the gas burette B to the reaction vessel; this was done as quickly as possible and any single admission could be carried out within 5 secs. the initial time of the experiment being taken as the average time between the commencement and the end of the admission. When the gases had reacted for a known time they were removed for analysis by opening the tap T, and expanding to the large evacuated volume V of the Toepler pump. The reaction was thus immediately stopped and the sample in V was analysed for carbon dioxide by potash absorption. (Since nitrous oxide is slightly soluble in caustic potash, the potash used was previously saturated with nitrous oxide.)

In all cases the course of the reaction is shown by graphical representation of the amount of carbon dioxide formed, as a percentage of the theoretical amount required by the above equation.

## Part I.—Measurable Reaction.

The preliminary results obtained with vessel A showed that the rate of reaction was dependent on the condition of the surface. Starting from a clean air exposed surface, the activity of the surface increased slowly and finally settled down to fairly constant activity. No marked fluctuations were observed over long periods so long as air was prevented from contact with the surface and that the vessel was completely evacuated before each experiment; this usually required twenty minutes
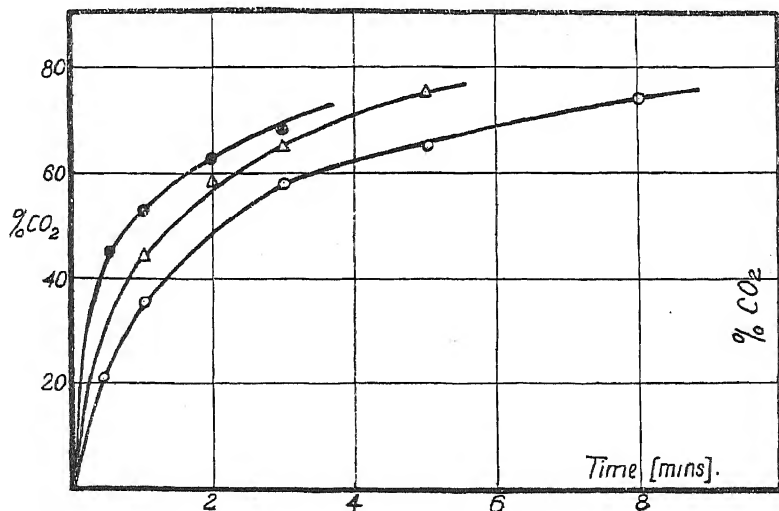


FIG. 2.—Influence of Pressure.
Mixture 1CO : 1N$_2$O.  Temperature 548° C.
Initial Pressure.  Curve I.  9·70 cms.
,, II.  11·90 ,,
,, III.  15·30 ,,

pumping. No change of pressure was observed during the reaction (at the temperatures employed no measurable decomposition of the nitrous was observed) and analysis of the resultant gases failed to show the presence of nitric oxide or any other oxides of nitrogen. Without applying any correction for the small amount of gas external to the furnace, it was found that at *circa* 550° C about 97 per cent. of the theoretical amount of carbon dioxide was formed within a comparatively short period.

**Order and Course of Reaction.**—The course of the reaction at 548° C. and for a series of different initial pressures of a 1 CO : 1$N_2O$ mixture is given in Fig. 2. The total order of the reaction as deduced from the influence of pressure on the initial rate of reaction was approximately 2 and this was so, even at pressures just below the explosion limit. The activation energy of the reaction as determined from the initial rate of reaction at a series of temperatures is equal to 22,000-23,000 Cals.

The effect of varying the initial concentration of the reactants (Fig. 3) throws much light on the nature of the reaction. The results may be summarised by saying that the 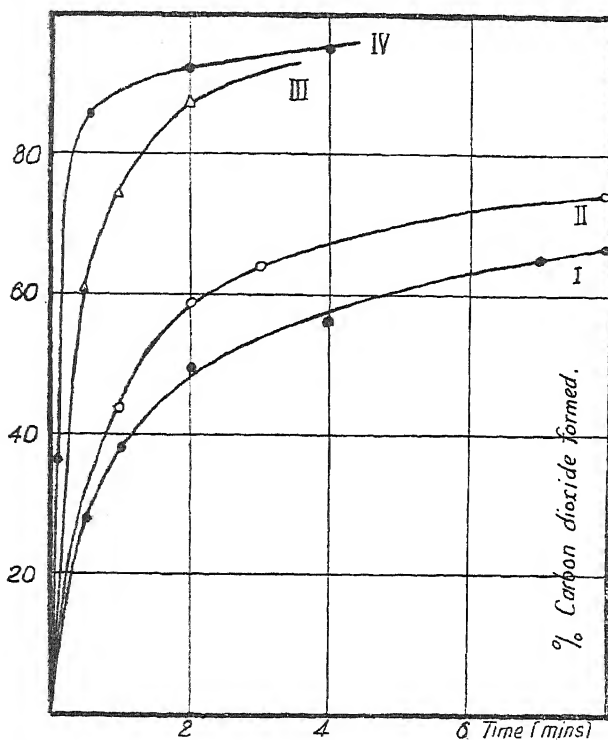rate of reaction is proportional to the initial concentration of the nitrous oxide and inversely proportional to the concentration of the carbon monoxide. This is a well-known type of surface reaction and means that the carbon monoxide is strongly adsorbed on the quartz surface compared with nitrous oxide. A similar kinetic expression has been found for the direct oxidation of carbon monoxide on quartz [4] and on platinum at low temperatures.[5]



FIG. 3.—Influence of excess $N_2O$ and CO. Temperature 548°.

| | | | |
|---|---|---|---|
| Curve | I. | Pressure $N_2O$ 3·63, CO 11·21 cms. | |
| „ | II. | „ $N_2O$ 3·61, CO 3·61 | „ |
| „ | III. | „ $N_2O$ 3·63, CO 1·21 | „ |
| „ | IV. | „ $N_2O$ 5·31, CO 1·81 | „ |

**Influence of Surface.** — The heterogeneous nature of the slow reaction was confirmed by studying the effect of increased surface on the reaction. This was investigated by packing the reaction vessel with small pieces of quartz tube. A very marked increase in the rate of reaction was observed. At 550° C. when the normal measurable reaction was slow, with the packed bulb the reaction was 90 per cent. complete within a ¼ minute, and it was only by lowering the temperature to 400° C. that the reaction proceeded at a rate suitable for measurement. Typical rate curves are shown in Fig. 4.

**Addition of the Inert Gases.**—Although the addition of argon, nitrogen and helium have a pronounced effect on the explosive part of the reaction (see later) these gases were found to be without appreciable

[4] Bodenstein and Ohlmer, *Z. physik. Chem.*, **53**, 166, 1907.
[5] Langmuir, *Trans. Faraday Soc.*, **17**, 621, 1922.

influence on the measureable part of the change (Fig. 5). The small in-
crease or decrease observed with added helium or nitrogen can be attributed to a slight change in the activity of the surface during the experiments. These observations support the view that the slow reaction is probably confined to the surface of the vessel, and if it does involve chains these must be very short.

**Addition of Nitric Oxide and Carbon Dioxide.**



Curve             Fig. 4.—Effect of Surface.           Pressure
I. Packed Vessel.   Temperature 429° C.      10·76 cms.
II.    „       „            „        409° C.      14·22   „
III. Unpacked  „            „        556° C.      14·47   „

—If the mechanism of measurable reaction is that suggested, it would be expected that small amounts of added carbon dioxide would have a similar influence to that of nitrogen. However, it was found that carbon dioxide produced a



Fig. 5.—Influence of Inert Gases.

I. 2CO : 2N₂O : 1N₂ mixture. Initial Pressure 13·63 cms.   Temperature 566° C.
II. 2CO : 2N₂O         „            „        13·40  „             „        565° C.
III. 2CO : 2N₂O        „            „        15·74  „             „        556° C.
IV. 2CO : 2N₂O : 1He   „            „        16·40  „             „        556° C.

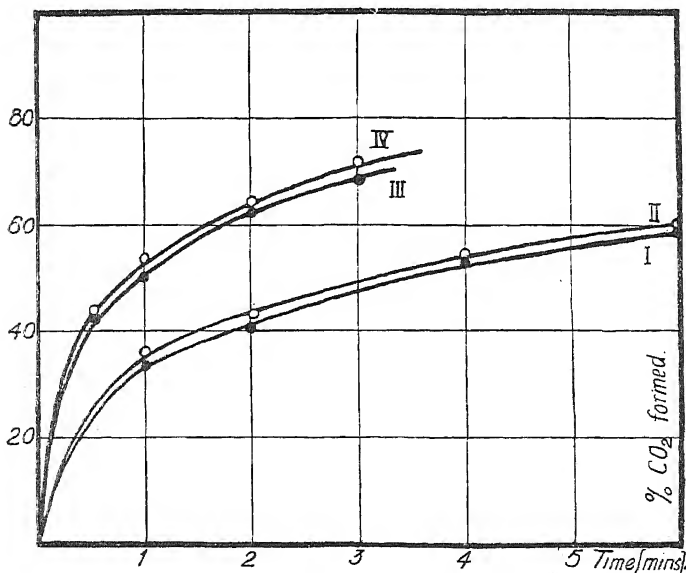remarkable increase in the rate of the slow reaction. Some typical results are given in Fig. 6. Since carbon dioxide is a product of the reaction, a similar autocatalysis must occur during the normal slow reaction, and the form of the rate curves (Fig. 3) suggest that this takes place. Comparison of the curves 1 and 3 of Fig. 6 (rate with and without carbon dioxide) shows that the influence of carbon dioxide is most effective during the initial
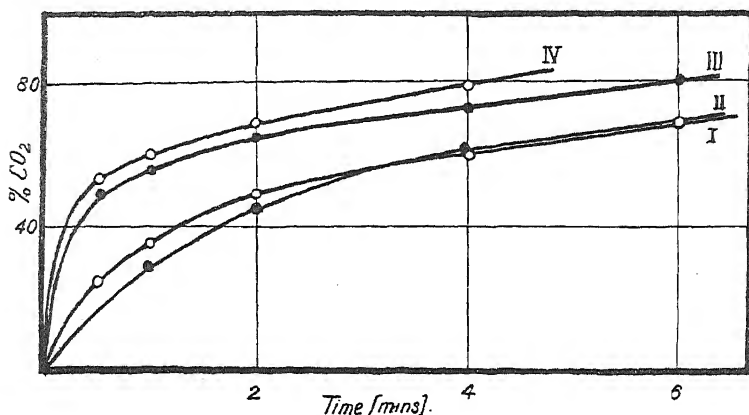


FIG. 6.—Influence of Carbon Dioxide and Nitric Oxide.

| | | | | | |
|---|---|---|---|---|---|
| I. $1CO : 1N_2O$. | | Initial Pressure 10·00 cms. | Temp. | 578° C. |
| II. $1CO : 1N_2O + 3$ per cent. NO. | ,, | 10·00 | ,, | ,, | 578° C. |
| III. $1CO : 1N_2O + 16·4$ per cent. $CO_2$. | ,, | 10·48 | ,, | ,, | 578° C. |
| IV. $1CO : 1N_2O + 14·4$ per cent. $CO_2$. | ,, | 9·16 | ,, | ,, | 581° C. |

part of the reaction ; the parallelism of the curves during the later stages indicate that the carbon dioxide produced by the reaction is equally effective in catalysing the change.

Small amounts of nitric oxide on the other hand appears to have little influence on the reaction (Fig. 6) other than an apparent slight inhibiting action during the initial stages of the reaction.

## Part II.—The Explosive Oxidation.

If the pressure of the gas exceeds a certain critical value, the measureable reaction gives way to explosive oxidation. In this case the oxidation did not proceed as represented by the simple equation :—

$$N_2O + CO \rightarrow CO_2 + N_2,$$

but considerable amounts of nitrogen oxides were formed, and also a decomposition of nitrous oxide occurred at the higher temperature produced. A pressure change thus occurred on explosion and since the volume of the parts of the system had been accurately calibrated any immediate combustion could be determined. Furthermore, the reaction showed a very marked induction period, and it was possible to observe the explosion directly by movement of the mercury meniscus of the manometer and also by the bright flame in the connecting tube. This was also supplemented by analysis if necessary. The experimental procedure was as in the previous part ; known amounts of the gas mixture were admitted from the gas burette to the reaction vessel, as quickly as possible and the occurrence of explosion observed in the manner described. The lower limiting pressure for explosion was approached from both sides.

The induction period which preceeded the explosion varied from less than a second to about 7 seconds depending on the temperature and the pressure of the gas. Attempts were made to determine the nature of the

change which occurred during the induction period and although the shortness of the period rendered this difficult some definite evidence was obtained which showed that a marked slow reaction was occurring. For instance, in one experiment, the gas mixture was admitted very quickly (1-2 secs.) by keeping the gas in the burette B under pressure, when the process of admitting the gas was reduced to merely opening the tap $T_2$. Mercury was prevented from entering the reaction vessel by means of the capillary trap, F. (1. c.c. vol.). The gas was removed after 3 secs. (time by an independent observer with a stopwatch) almost instantaneously by opening T, and expanding to V as before.

At 553° C. and 20 cm. pressure the mean induction period was 4 seconds ; analysis of the gases removed after 3 secs. showed that about 4-5 per cent. reaction had occurred. This is about the same as occurred by the slow reaction under these conditions. (Blank analysis of the mixture proved the absence of carbon dioxide or other adsorbed gas.) It is clear that there is no rapidly accelerating reaction taking place during the induction period which leads to a thermal explosion, but that the slow reaction passes abruptly into explosion. This is supported by other evidence.

**Lower Explosion Limit.** — The position of the lower limit could be determined very sharply and showed little tendency to shift even over many series of experiments. However, as the experiments extended over many months and since the whole phenomenon is intimately connected with a surface reaction, it was only to be expected that variations of the limit would eventually be observed. It was therefore necessary to check frequently the activity of the surface and in all series, the results were checked against a standard 1 $N_2O$ : 1 CO mixture. The influence of varying the composition of the mixture shows that the ignition temperature is lowered by both excess carbon monoxide and nitrous oxide (Fig. 7). From this it appears that the explosion is facilitated by increased concentration of carbon monoxide. This is the opposite of the effect of carbon monoxide on the slow reaction, and indicates that the measurable and explosive reactions follow entirely different mechanisms.
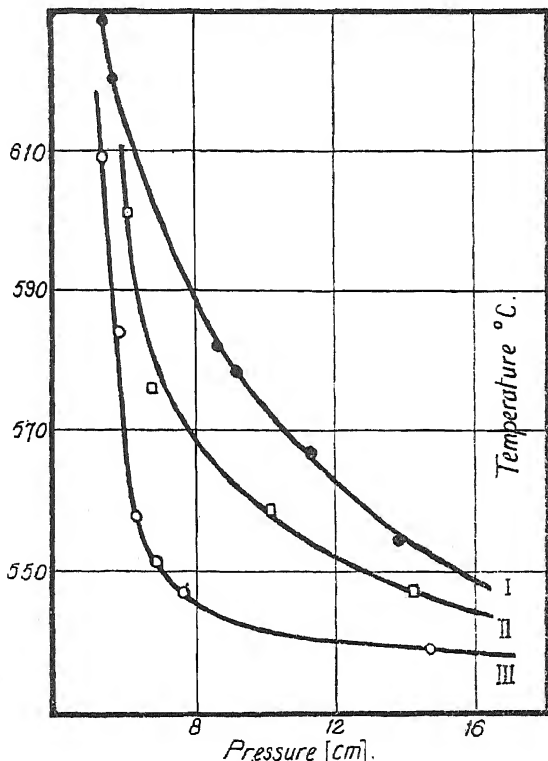


· Fig. 7.—Lower Explosion Limit.
Curve   I. $1N_2O$ : $1CO$   mixture.
  „      II. $1N_2O$ : $2CO$       „
  „     III. $3N_2O$ : $1CO$       „

**Influence of Added Gases.**—In contrast to the accelerating influence of carbon dioxide on the slow reaction this gas appears to be without effect on the explosive reaction. On the other hand, the influence of nitric oxide on the ignition phenomena is of significance. The effect of 2 per cent. added nitric oxide was to cause an increase of 20 cms. in the limiting pressure for explosion, and 3 per cent. inhibiting explosion entirely up to pressures of 30 cm. Since this gas was without influence on the surface part of the reaction these observations suggest that the explosion is determined by a reaction chain mechanism.

The influence of inert gases is more complex. Helium caused a large increase in the partial pressure of the gases required to bring about explosion, nitrogen produced a much smaller increase, whilst argon lowered the partial pressure for explosion. These results are shown graphically in
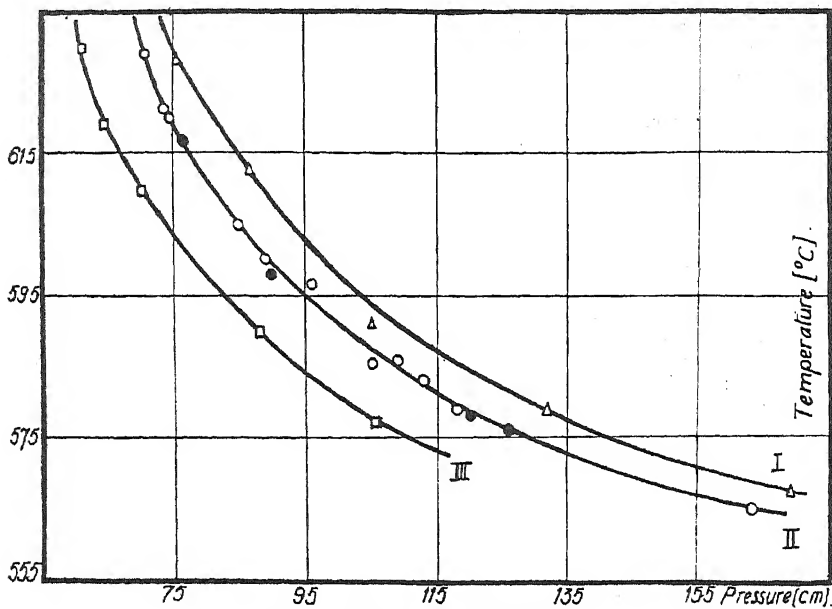


Fig. 8.—Influence of Inert Gases.

Curve   I. △ 2CO : 2N₂O : 1N₂ mixture.
  ,,    II. ◯ 1CO : 1N₂O.   ● 1CO : 1N₂O + 14 per cent. CO₂.
  ,,    III. ☐ 1CO : 1N₂O : 1A.

Figs. 8 and 9. In each case besides the usual control experiments, the position of the limit was checked by introducing a known percentage of inert gas into the blank mixture.

The facts may be summarised as follows :—

(1) The slow reaction in the initial stages is a surface reaction retarded by the carbon monoxide. This reaction is catalysed by the addition of carbon dioxide and by the carbon dioxide formed during the reaction.

(2) The slow reaction passes abruptly into explosion above a certain critical pressure.

(3) The lower explosion limit decreases with increase in temperature and also by the addition of excess carbon monoxide and nitrous oxide.

(4) A slow rate of surface reaction corresponds to a high ignition pressure.

(5) The presence of inert gases is to increase or decrease the lower limit and this is probably determined by the physical properties of the gas employed.
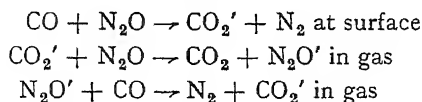
(6) The addition of a small amount of nitric oxide inhibits the explosion.

### Discussion.

### 1. Slow Reaction.

The relationship found for the rate of the slow reaction together with the large effect produced by added surface indicate that in the initial stages the reaction is purely heterogeneous. The slight inhibitive action of small amounts of nitric oxide is readily understandable on this view. The autocatalytic effect of carbon dioxide, however, is not so easily explained by any hypothesis of heterogeneous reaction. It may be imagined that the adsorbed carbon dioxide molecules act as acceptors of energy and that this energy may readily be transferred to the nitrous oxide molecules. This transfer may occur directly at the surface or by collision of nitrous oxide molecules with the adsorbed carbon dioxide molecules.



Fig. 9.—Lower Explosion Limit ; Influence of Helium.

| | | | |
|---|---|---|---|
| Surface A. | Curve | I. | $1CO : 1N_2O$ mixture. |
| | ,, | III. | $1CO : 1N_2O : 1He$ mixture. |
| Surface B. | ,, | II. | $1CO : 1N_2O$ mixture. |
| | ,, | IV. | $2CO : 2N_2O : 1He$. |

On the other hand the autocatalysis of the reaction by the carbon dioxide formed is most easily understood by the hypothesis of a chain reaction. The following series of processes may be assumed to occur :—

$$CO + N_2O \rightarrow CO_2' + N_2 \text{ at surface}$$
$$CO_2' + N_2O \rightarrow CO_2 + N_2O' \text{ in gas}$$
$$N_2O' + CO \rightarrow N_2 + CO_2' \text{ in gas}$$

or possibly an atomic chain mechanism may be set up and this will be discussed later. Such a transfer of energy between carbon dioxide and nitrous oxide molecules is possible as has been shown by the work of Volmer and his co-workers [6] who have studied the effect of carbon dioxide on the unimolecular decomposition of nitrous oxide. These workers found that carbon dioxide was the most effective gas in maintaining the unimolecular rate and was more effective than nitrous oxide itself. How-

[6] Volmer and Kummerow, *Z. physik. Chem.*, **9B**, 141, 1930 ; Nagasako and Volmer, *ibid.*, **11**, 420, 1931 ; Volmer and Froelich, *ibid.*, **19**, 89, 1932 ; Volmer and Bogdan, *ibid.*, **21**, 271, 1933.
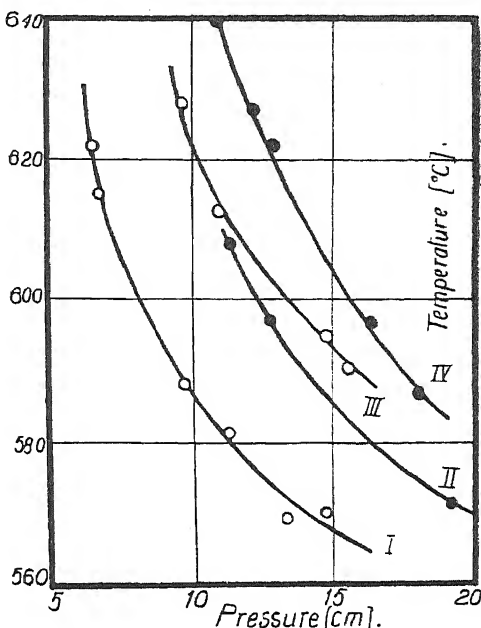
ever, the influence of added inert gases or the effect of surface, supplies no evidence for the existence of reaction chains. This is probably due to the shortness of the chain length since comparison of the initial rates of reaction of a $1\ CO : 1\ N_2O$ mixture, with and without added carbon dioxide, and assuming that the normal slow reaction is a surface reaction, shows that the chain length is of the order of 15 molecules.

The investigation of the reaction at a pressure just below the explosion limit show that there is no marked change in the nature or mechanism of the slow reaction in this region ; that is, the measureable reaction passes almost abruptly into explosion as the pressure is increased.

## 2. The Lower Explosion Limit.

The explanation of the existence of a lower explosion limit has been given previously by many investigators. However, in order to obtain a clear understanding of the present problem, it is necessary to reconsider briefly some of these theories. There are two types of phenomenon which give rise to explosion, firstly, the self acceleration of the reaction according to the classical theory when the rate of production of heat by the reaction is greater than that lost to the walls, and secondly, the occurrence of branching chains.

The investigations of a large number of such reactions has revealed the interesting fact that in almost every case the explosion originates more easily from a surface. This is usually the source of explosion in investigations carried out in heated quartz vessels, as in the present experiments. The reaction may originate from the surface in many ways and these may conveniently be considered as being of two types : (1) As a result of the surface reaction energy rich molecules or atoms (carriers of the chain) are injected into the gas and these set up the chain branching if the conditions are favourable. (2) The surface reaction may be normal thermal reaction confined to the surface film and this may either set up chains in the layers adjacent to the wall on account of the high temperature in the surface film, or give rise to a truly thermal explosion independent of the existence of reaction chains. Much information has been obtained on this point by investigations on the effect of the addition of inert and other gases to the explosive mixture and in this respect the present problem is of special interest. The following cases may be considered :—

(1) (*a*) The ideal case is that of an atomic chain initiated at the surface and broken only by the surface. The presence of inert gas will then act solely so as to increase the length of the chains by hindering diffusion to the wall, and the lower limit will be decreased.[7]

(*b*) The chain may be initiated by an unstable molecule such as a peroxide which is formed at the wall and diffuses into the gas. Collision with an inert gas then may deactivate this unstable molecule, the effectiveness being determined by the probability of energy transfer between the molecules. The presence of inert gas would then cause an increase in the explosion limit, and this is found in the oxidation of carbonyl sulphide [8] and dimethyl zinc [9]

(*c*) The reaction chains may be set up by a " thermal " surface reaction and this can lead to explosion only when the temperature of

[7] Semenoff.   Ref. 1, Hinshelwood and Dalton, *Proc. Roy. Soc.*, **125A**, 294, 1929, by Melville and Ludlam, *Proc. Roy. Soc.* **1932A**, 108, 1931.

[8] Bawn, *J. Chem. Soc.*, 146, 1933.

[9] Thompson and Kelland, *J. Chem. Soc.*, 756, 1933.

the layers exceed a certain critical value—the ignition temperature of the gas. The influence of an inert gas will, as pointed out by Garner,[3] be twofold : (1) it will tend to lower the temperature of the surface film by virtue of its specific heat and thermal conductivity. (2) Compress the reaction chains to within a shorter distance of the wall by an effect similar to (a). The second factor will cause an increase in the temperature of the surface film, and may raise it to the ignition temperature ; in such cases the influence of the inert gas will be to reduce the partial pressure of the gas necessary for explosion. On the other hand, the effect (a) will tend to decrease the ease of explosion and it is clear that with a series of inert gases the magnitude of the effect will depend essentially on the physical properties of the added gas. However, if both influences occur together, it is quite possible that the effect may change from positive to negative as one passes from helium with high thermal conductivity and diffusion coefficient to a heavy inert gas like krypton.

(d) In the case of the truly thermal explosion the governing factor will be the rate of conduction of heat away from the reaction zone to the walls ; the more rapidly this occurs the higher the explosion limit and in this case the raising of the limit due to the presence of inert gases would be proportional to the conductivity of the gas.

It is obvious that of the above possibilities, only (c) or (d) can provide a satisfactory explanation of the results described.

The varied action of inert gases and also of the existence of reaction chains suggests that explanation (c) is the more probable, i.e., the chains are initiated in the surface layer by a thermal reaction occurring at the surface.

The large increase in the explosion limit produced by helium is due to the high rate at which this gas transfers heat from the surface film. The thermal conductivity of argon is much lower than that of helium, and it was therefore to be expected that this gas would cause a smaller increase in the explosion limit. The fact that argon actually lowers the limit indicates that the second factor—the compression of the reaction chains to within a smaller distance of the surface—is effective.

The slightly increased effect of nitrogen compared to that of argon is due to the higher specific heat of nitrogen which causes a further lowering of the temperature of the film. The observation that carbon dioxide was without influence on the limit may result from the balancing influence of the opposing effects discussed above.

Further information as to the influence of inert gases is obtained from a study of the induction period.

The induction period may have either a thermal or chain origin. According to the latter theory it is the time required for the chain to build up and may be of considerable length especially if any intermediate product in the chain has a definite life period. On the other hand, if the initiation of the chain is determined by a thermal reaction, that is the self-heating of the mixture until the ignition temperature is reached, the induction period is simply the time required for the surface reaction to raise the temperature of the gas to the necessary value. The induction period will not be constant but will be determined by the initial rate of reaction and thus by the relative adsorbabilities of the reactants and by the presence of diluent gases. It was found in these experiments that the induction period was very short if the pressure of the gas was well above the explosion limit, but increased considerably as the pressure was

reduced. This could usually be taken as a clear indication of the where-abouts of the limiting pressure. Also in the presence of helium gas the induction period was increased considerably, and this may be interpreted as due to the high thermal conductivity of this gas which produces a marked lowering of the temperature of the surface layers. It is possible that this may also explain the effect of helium in raising the explosion limit.
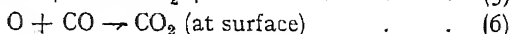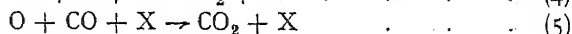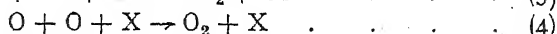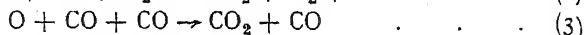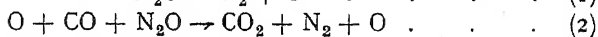
**Influence of Added Nitric Oxide.**—The influence of small amounts of nitric oxide on the explosive reaction indicates a chain reaction. Whereas nitric oxide was without appreciable influence on the slow surface reaction, the explosive reaction was completely inhibited when the concentration of nitric oxide exceeded 3 per cent. The nitric oxide appears, therefore, to function as a chain breaker in the gas or the catalysis may be entirely a wall effect, although there is no experimental evidence for the latter. Many mechanisms may be suggested and it seems most probable that the nitric oxide functions by removing oxygen atoms from the chain. The following reactions may occur:—

$$O + NO + X \rightarrow NO_2 + X \qquad . \qquad . \qquad . \qquad (1)$$
$$NO_2 + N_2O \rightarrow 2NO + O \qquad . \qquad . \qquad . \qquad (2)$$
$$NO_2 + O \rightarrow NO + O_2 \qquad . \qquad . \qquad . \qquad (3)$$
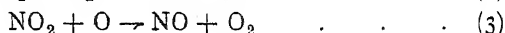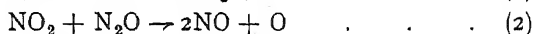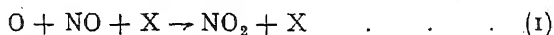
It is known that at the temperature of the experiments (3) is very effective in removing oxygen atoms.[10]

**Reaction Mechanism.**—The slow oxidation is a surface reaction which passes abruptly into explosion above a certain critical pressure. It is shown that this occurs on account of the exothermic nature of the surface reaction. The evidence indicates the presence of chains, these are probably initiated by oxygen atoms produced by the thermal decomposition of nitrous oxide. This takes place in the surface layers where a higher temperature exists.

The following cycle of changes account for the observed phenomena :—

$$N_2O \rightarrow N_2 + O \qquad . \qquad . \qquad . \qquad . \qquad (1)$$
$$O + CO + N_2O \rightarrow CO_2 + N_2 + O \qquad . \qquad . \qquad . \qquad (2)$$
$$O + CO + CO \rightarrow CO_2 + CO \qquad . \qquad . \qquad . \qquad (3)$$
$$O + O + X \rightarrow O_2 + X \qquad . \qquad . \qquad . \qquad (4)$$
$$O + CO + X \rightarrow CO_2 + X \qquad . \qquad . \qquad . \qquad (5)$$
$$O + CO \rightarrow CO_2 \text{ (at surface)} \qquad . \qquad . \qquad (6)$$

Reaction (1) is more probable than $N_2O \rightarrow N + NO$ and requires an energy of 53,000 Cals. Reaction (4), (5) and (6) terminate the chain, (6) which occurs at the surface being the most effective. This also accounts for the lower limiting pressure. There is also the possibility of the following chain :—

$$N_2O + CO \rightarrow CO_2' + N_2 \text{ (at surface)} \qquad . \qquad (7)$$
$$CO_2' + N_2O \rightarrow N_2O' + CO_2 \qquad . \qquad . \qquad (8)$$
$$N_2O' + CO \rightarrow N_2 + CO_2' \qquad . \qquad . \qquad . \qquad (9)$$
$$N_2O \rightarrow N_2 + O \qquad . \qquad . \qquad . \qquad (10)$$
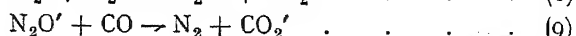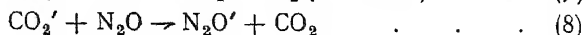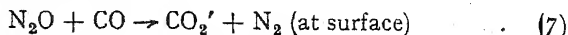
Neither these chains processes, alone, can lead to an explosion. It is only on account of the exothermic nature of one or more of the elemen-

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[10] Farkas and Harteck, *Nature*, **126**, 351, 1930.

tary reactions which lead to a self-acceleration of the total reaction that the gases ignite. Any factor which influences either of the above processes will automatically change the explosion limit. Thus the addition of an inert gas which facilitates the transfer of heat from the reaction zone or of nitric oxide which inhibits one of the reactions cause an increase in the lower limiting pressure necessary for explosion.

## Summary.

(1) The oxidation of carbon monoxide by nitrous oxide in quart vessels and in the neighbourhood of 550° C. is a surface reaction, the rate of which is given by the relationship $dx/dt = k \ N_2O/CO$, *i.e.*, the carbon monoxide is strongly adsorbed. The reaction is not influenced by the addition of inert gases or nitric oxide, has only a slight retarding action. Added carbon dioxide produced a remarkable increase in the rate. Carbon dioxide formed during the reaction, also exerts a catalytic effect, and this is attributed to a chain reaction.

(2) Between certain limits of pressure and temperature the slow reaction passes into explosion. The lower explosion limit is decreased by excess carbon monoxide and nitrous oxide. It is affected by the presence of inert gases in such a way as to show that it is governed by the temperature of the surface layers. Small amounts of nitric oxide inhibit the explosion.

(3) The observed phenomena can be explained by the assumption that the oxidation is a chain reaction, which leads to a thermal explosion. The chains are initiated from the layers adjacent to the walls. A mechanism of the chemical changes involved has been suggested.

*The University,*
*Manchester.*

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# THE DISSOCIATION PRESSURES OF SOME SALT HYDRATES.

By D. G. R. Bonnell and L. W. Burridge.

The various methods which have been applied from time to time to measure the dissociation pressures of salt hydrates have been described by several investigators, and in the present investigation it was decided that the dynamic method, as employed by Partington,[1] was the most suitable. In this method a volume of thoroughly dried air is passed successively over the salt hydrate, through phosphorus pentoxide tubes, a water saturator and finally another phosphorus pentoxide tube. If the hydrate and water saturator are maintained at the same constant temperature and the rate of passage of air sufficiently slow to ensure equilibrium with the water vapour, then the weights of water absorbed in the respective phosphorus pentoxide tubes will be directly proportional to the vapour pressures of the salt hydrate and of the pure water.

[1] Partington, *J. Chem. Soc.*, **99**, 467, 1911.

## Experimental.

The general lay-out of the apparatus is shown diagrammatically in Fig. 1. A current of air (about one to two litres per hour) from a constant pressure reservoir and dried by passing over sulphuric acid, calcium chloride and phosphorus pentoxide was brought to the temperature of the bath by passing through a copper preheater completely immersed in the thermostat. The air then passed through a further phosphorus pentoxide tube and entered the salt saturator, which was of a similar form to that used by Partington. On leaving this saturator, the air passed through a phosphorus pentoxide absorption tube which removed the water vapour extracted from the salt. The connection between the saturator and the absorption tube was made by means of a U tube fitted with mercury seals and a differential manometer, as shown in Fig. 1. This arrangement permitted the easy removal and replacement of the absorption tube when a weighing was necessary while the manometer showed the difference in pressure between the external atmosphere and the air-water vapour mixture inside the saturator. All traces of mercury were completely removed from the arms of the tube previous to weighing against a counterpoise of practically identical form and weight.

The dried air, after leaving the first absorption tube, passed into a water vapour saturator and thence by the same connection arrangement to a second absorption tube. The path between this saturator and the absorp-



DRY AIR SUPPLY

TO BACK DIFFUSION TRAP AND GAS METER

P₂O₅ DRYING TUBE

P₂O₅ ABSORPTION TUBE I

P₂O₅ ABSORPTION TUBE II

MERCURY SEALS

MERCURY SEAL WITH MANOMETER I

PREHEATER

SALT SATURATOR

WATER SATURATOR

MERCURY SEAL WITH MANOMETER II
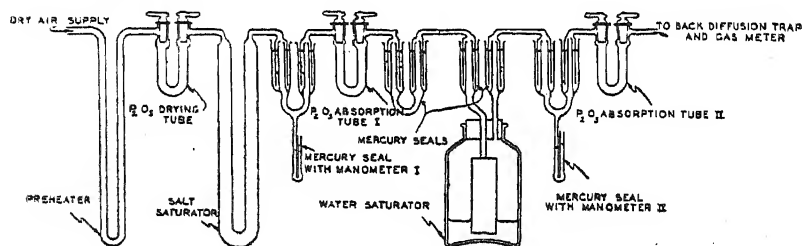
FIGURE I

tion tube was kept at a temperature of about 35° C., by means of electrical heaters, so that all tendencies towards condensation were eliminated. The preheater, salt and water saturators were immersed in a water thermostat kept constant to ± 0·04° C., while the absorption tubes with the mercury seal connections were fixed to the outer side of the bath.

The preparation of a water vapour saturator in which complete saturation of the air is obtained, without the formation of a fine water spray, is always difficult, but spray formation was successfully overcome in this investigation in the following manner :—

A roll of ashless filter paper was wound around a glass tube provided with an aperture A on one side, as shown in Fig. 2. The winding was so arranged that alternate walls and spaces were formed in the roll, which was bound by two bands of pure copper wire along BC and FG and then sterilised by heating for some hours in an air-bath at 100° C. The upper surface of the roll above band BC was carefully covered with paraffin wax in order to avoid any air leakages through the paper joints at this surface. Care must be taken during this operation to avoid the hot wax from penetrating too far down the roll. The whole was now sealed (as shown in Fig. 2) in a glass bottle which contained some freshly distilled water. The quantity of water present was adjusted to within about 1 inch of the lower limit of the cavities in the roll and due to the surface tension the water rose in the paper and thereby thoroughly wetted the walls.

Air entering the bottle through the tube at E must travel along the path indicated by the arrows in Fig. 3 and is therefore in contact with the saturated walls for the whole length of the roll before it can pass out through the outlet tube at O. In this way complete saturation of the air was ensured without any danger of spray formation. The water removed from the paper was continuously replaced by water from the lower reservoir by capillary forces.

Previous to the dissociation pressure determinations a series of tests was carried out to investigate the efficiency of such a saturator. This was done by utilising it for the determination of the vapour pressure of water by passing a known volume of dry air through and weighing the amount of water taken up. The results gave an average value of 12·80 mm. for 15° C. and 17·60 mm. for 20° C. as compared with 12·788 mm. and 17·535 mm. given in the International Critical Tables.

For the preparation of the hydrates, salts of A.R. purity were recrystallised at the appropriate temperature. In each case the material placed in the salt saturator was an intimate mixture of the hydrate pair investigated.

## Results.

The dissociation pressures of the hydrates were calculated from the weights of water in the two phosphorus pentoxide tubes as follows :—

Let $w_1$ and $w_2$ be the weight in grams of water absorbed from the water and from the salt when $V$ litres of dry air, at atmospheric pressure $P$, are passed through the system.

$h_1$ and $h_2$ are the positive pressures shown by the manometers connected to the water and salt saturators respectively.

$p_s$ is the saturation vapour pressure of water and $p_a$ the dissociation pressure of the salt hydrate.



FIG. 2.



FIGURE 3    SECTION OF SATURATOR AT S-T (FIG 2)

The volume $V$ when under the pressure inside the water saturator occupies the volume $\dfrac{VP}{P + h_1 - p_s}$. The weight of water vapour contained in this volume when saturation is obtained is

$$\left( \frac{VP}{P + h_1 - p_s} \cdot \frac{p_s}{760} \cdot \frac{273}{273 + t} \right) \cdot d,$$
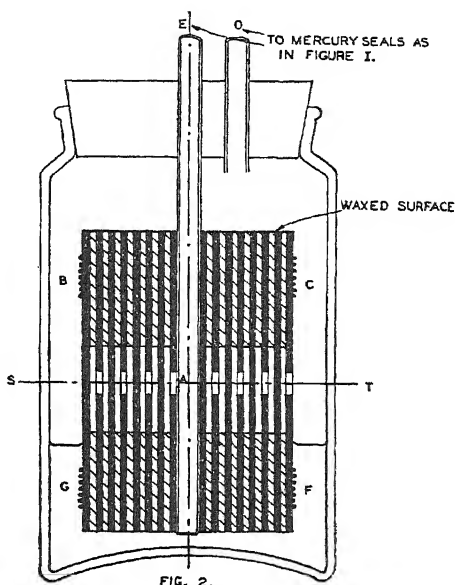
where $d$ = weight of 1 litre of water vapour at 760 mm. and 0° C. and $t$ is the temperature of the thermostat.

$$\therefore \left( \frac{VP}{P + h_1 - p_s} \cdot \frac{p_s}{760} \cdot \frac{273}{273 + t} \right) d = w_1$$

similarly for the salt and saturator it can be shown that

$$\left( \frac{VP}{P + h_2 - p_a} \cdot \frac{p_a}{760} \cdot \frac{273}{273 + t} \right) d = w_2$$

then

$$\frac{w_1}{w_2} = \frac{P_s}{p_a} \cdot \frac{P + h_2 - p_a}{P + h_1 - p_s}$$

$$P_a = \frac{\frac{w_2}{w_1} \cdot (P + h_2)}{\frac{P + h_1 - p_s}{p_s} + \frac{w_2}{w_1}}$$

$$= \frac{\frac{w_2}{w_1} \cdot p_s \cdot (P + h_2)}{P + h_1 - p_s + \frac{w_2}{w_1} \cdot p_s}.$$

The values for $p_1$ were taken from International Critical Tables. The results obtained are given in the table.

## TABLE I.

Temp.    Dissociation pressures determinations in mm. of Hg.

### $ZnSO_4 7H_2O - 6H_2O$.

| Temp. | | | | | | | | | Mean | |
|---|---|---|---|---|---|---|---|---|---|---|
| 10° | 4·54, | 4·41, | 4·50, | 4·48, | 4·46, | | | | Mean | 4·48 |
| 15° | 6·92, | 6·92, | 6·91, | 6·85, | 6·86, | 6·88 | | | ,, | 6·89 |
| 20° | 10·22, | 10·32, | 10·32, | 10·23, | 10·43, | 10·43 | | | ,, | 10·33 |
| 25° | 15·39, | 15·40, | 15·48, | 15·33, | 15·34, | 15·47, | 15·44 | | ,, | 15·38 |

### $ZnSO_4 6H_2O - 5H_2O$.

| Temp. | | | | | | | | | Mean | |
|---|---|---|---|---|---|---|---|---|---|---|
| 10° | 4·37, | 4·37, | 4·37, | 4·35, | 4·35, | 4·38, | 4·37, | 4·37 | Mean | 4·36 |
| 15° | 6·57, | 6·60, | 6·62, | 6·62, | 6·64, | 6·63, | 6·56, | 6·62 | ,, | 6·61 |
| 20° | 9·85, | 9·83, | 9·87, | 9·83, | 9·84, | 9·77, | 9·72, | 9·88 | ,, | 9·82 |
| 25° | 14·22, | 14·12, | 14·26, | 14·35, | 14·34, | 14·06, | 14·32, | 14·24 | ,, | 14·24 |

### $FeSO_4 7H_2O - 6H_2O$.

| Temp. | | | | | | | | | Mean | |
|---|---|---|---|---|---|---|---|---|---|---|
| 10° | 4·62, | 4·55, | 4·66, | 4·58, | 4·56, | 4·57, | 4·54, | 4·67 | Mean | 4·59 |
| 15° | 6·81, | 6·79, | 6·82, | 6·78, | 6·76, | 6·77, | 6·84, | 6·87 | ,, | 6·80 |
| 20° | 10·16, | 10·16, | 10·15, | 10·14, | 10·09, | 10·16, | 10·05, | 10·26 | ,, | 10·15 |
| 25° | 14·62, | 14·66, | 14·67, | 14·45, | 14·46, | 14·45, | 14·52 | | ,, | 14·55 |

### $MgSO_4 7H_2O - 6H_2O$.

| Temp. | | | | | | | | | Mean | |
|---|---|---|---|---|---|---|---|---|---|---|
| 10° | 2·93, | 2·93, | 3·04, | 2·97, | 2·95, | 3·17 | | | Mean | 3·0 |
| 15° | 5·11, | 5·02, | 4·99, | 5·04, | 5·08, | 5·03, | 5·02, | 5·04 | ,, | 5·04 |
| 20° | 7·98, | 7·97, | 7·92, | 7·86, | 7·92, | 7·92, | 7·94, | 7·86 | ,, | 7·92 |
| 25° | 12·14, | 12·04, | 12·16, | 12·18, | 12·07, | 12·13 | | | ,, | 12·12 |

### $Na_2H PO_4 7H_2O - 2H_2O$.

| Temp. | | | | | | | | | Mean | |
|---|---|---|---|---|---|---|---|---|---|---|
| 10° | 4·57, | 4·57, | 4·55, | 4·56, | 4·54, | 4·53, | 4·56 | | Mean | 4·55 |
| 15° | 6·82, | 6·81, | 6·81, | 6·79, | 6·80 | | | | ,, | 6·81 |
| 20° | 10·08, | 10·03, | 10·11, | 10·04, | 10·02, | 9·98, | 10·06, | 10·02 | ,, | 10·04 |
| 25° | 14·44, | 14·38, | 14·43, | 14·32, | 14·46, | 14·47 | | | ,, | 14·41 |

### $NiSO_4 7H_2O - 6H_2O$.

| Temp. | | | | | | | | | | Mean | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10° | 6·92, | 6·88, | 6·83, | 6·83 | | | | | | Mean | 6·87 |
| 15° | 10·30, | 10·38, | 10·32, | 10·36, | 10·33, | 10·34 | | | | ,, | 10·34 |
| 20° | 14·74, | 14·79, | 14·77, | 14·67, | 14·86, | 14·76, | 14·77, | 14·90 | | ,, | 14·78 |
| 25° | 20·86, | 20·58, | 21·52, | 21·90, | 21·18, | 20·83, | 21·56, | 21·36, | 21·50 | ,, | 21·15 |

In Table II. the values obtained in this investigation are compared with those obtained at 25° C. by other investigators.

TABLE II.

| Author. | Vapour Pressure at 25° C. | | | | | |
|---|---|---|---|---|---|---|
| | $ZnSO_4$ $7-6H_2O.$ | $ZnSO_4$ $6-5H_2O.$ | $FeSO_4$ $7-6H_2O.$ | $MgSO_4$ $7-6H_2O.$ | $Na_2H\,PO_4$ $7-2H_2O.$ | $NiSO_4$ $7-6H_2O.$ |
| Frowein [2] . | 14·7 | 13·29 | | 12·17 | | |
| Schumb [3] . | 15·34 | | 14·56 | 12·50 | | 20·69 |
| Foote and Scholes [4] . | 13·6 | 12·8 | | 11·5 | 12·4 | |
| Lescoeur [5] . | 14·0 | | | 11·7 | | |
| Carpenter and Jette [6] . | | | | 12·7 | | |
| R. E. Wilson [7] | | | | | 14·51 | |
| Bolte [8] . . | | | | 12·0 | | |
| This investigation . . | 15·38 | 14·24 | 14·55 | 12·12 | 14·41 | 21·15 |

## Heats of Hydration.

By assuming that water vapour obeys the gas laws and that the heat of hydration is independent of the temperature, the heats of hydration can be calculated by means of the Clausius—Clapeyron equation. This can be written in the form :—

$$Q \text{ (gm. cals)} = 4\cdot576 \frac{T_2 T_1}{T_2 - T_1} \log \frac{\dfrac{p_a'}{p_s'}}{\dfrac{p_a}{p_s}}$$

$p_a$ and $p_a'$ are the dissociation pressures of the salt while $p_s$ and $p_s'$ are the saturation vapour pressures of water at the temperatures $T$ and $T_1$.

The values so calculated are given in Table III.

TABLE III.

| Reaction. | $Q$ (in g. Cals.) for Temperature Range. | | |
|---|---|---|---|
| | 20–25. | 15–20. | 10–15. |
| (a) $ZnSO_4\,7H_2O \rightarrow ZnSO_4\,6H_2O + H_2O$ (liq) . . | 3272 | 2994 | 3299 |
| (b) $ZnSO_4\,6H_2O \rightarrow ZnSO_4\,5H_2O + H_2O$ (liq) . . | 2196 | 2709 | 2866 |
| (c) $MgSO_4\,7H_2O \rightarrow MgSO_4\,6H_2O + H_2O$ (liq) . . | 4315 | 4568 | 6160 |
| (d) $FeSO_4\,7H_2O \rightarrow FeSO_4\,6H_2O + H_2O$ (liq) . . | 1994 | 2910 | 2210 |
| (e) $Na_2H\,PO_4\,7H_2O \rightarrow Na_2H\,PO_4\,2H_2O + 5H_2O$ (liq) | 10010 | 12160 | 12140 |
| (f) $NiSO_4\,7H_2O \rightarrow NiSO_4\,6H_2O + H_2O$ (liq) . . | 1898 | 1393 | 2608 |

[2] Frowein, *Z. physik. Chem.*, **1**, 1, 1887.
[3] Schumb, *J. Amer. Chem. Soc.*, **45**, 342, 1923.
[4] Foote and Scholes, *J. Amer. Chem. Soc.*, **33**, 1309, 1911.
[5] Lescoeur, *Ann. Chim. Physics* (6), **16**, 378, 1889.
[6] Carpenter and Jette, *J. Amer. Chem. Soc.*, **45**, 578, 1923.
[7] R. E. Wilson, *J. Amer. Chem. Soc.*, **43**, 704, 1921.
[8] H. Bolte, *Z. physik. Chem.*, **80**, 338, 1912.

Thomsen's experimental determinations give a value of 3420 g. cals for reaction (*a*) and 3700 g. cals for (*b*) above. These values are in fair agreement with the calculated values.

## Summary.

The dissociation pressures of disodium hydrogen phosphate, hepta hydrate, zinc sulphate, hexahydrate and the heptahydrates of the sulphates of zinc magnesium, nickel and ferrous iron have been determined at 10°, 15°, 20° and 25° C. by the dynamic method.

A new type of water vapour saturator, which removes the danger of spray formation, has been described.

The heats of hydration for the various reactions have been calculated from the dissociation pressure data by means of the Clausius—Clapeyron equation.

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# PURIFICATION AND PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS. VIII. A CONTRIBUTION TO THE THERMAL STUDY OF LIQUID CRYSTAL FORMATION.

By Evald L. Skau and Harry F. Meier.

The desirability of a careful study of the heat changes involved in the transition from the liquid-crystalline state to the amorphous liquid state * using compounds of unquestionable purity was pointed out by Bose [1] in 1907. Although calculated heats of transition of a few of these substances had been reported [2] and calorimetric measurements had been made [3] which showed fair agreement, Rotarski and Shemtschushny, [4] on the one hand, and de Kock, [5] on the other, gave conflicting reports on the cooling curve behaviour of such substances at the transition point. No further investigation was carried out along these lines until 1930, when it was shown definitely by Vorländer [6] that there was a sharp heat change at the transition point. From his differential heating curves, however, it was impossible to conclude whether or not the heat change took place at a constant temperature.

The present thermal study was made by means of an apparatus especially designed for obtaining carefully controlled heating and cooling curves. As has already been explained, this apparatus gives precise evidence as to the time-temperature curve behaviour and at the same time affords a means of determining with reasonable certainty the

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* This will be referred to throughout as the transition point.
[1] Bose, *Physik. Z.,* 8, 349, 1907.
[2] Hulett, *Z. physik. Chem.,* 28, 629, 1899 ; de Kock, *Z. physik. Chem.,* 48, 129, 1904 ; and others.
[3] Schenck, *Z. physik. Chem.,* 28, 280, 1899.
[4] Rotarski and Shemtschushny, *Chem. Zt.,* 28, 1108, 1904.
[5] de Kock, *Z. physik. Chem.,* 48, 129, 1904.
[6] Vorländer, *Physik. Z.,* 31, 428, 1930.

purity of the sample.* The curves obtained also give an indication of the relative magnitude of the heat changes at the melting-point and the transition point.[7]

*Para*-methoxycinnamic acid was synthesised by the Knoevnagel reaction from the best grades of anisaldehyde and malonic acid obtainable from Eastman Kodak Co.[8] The crude product was crystallised twice from 25 per cent. alcohol and once from 50 per cent. alcohol, and then dried in the oven at 110°. The samples were introduced into the freezing-point tubes in the usual way and sealed off *in vacuo*. It was found advisable to use a fresh sample for each determination, since the compound decomposed on heating as was shown by the evolution of carbon dioxide and the development of a discoloration in the otherwise colourless liquid.

While cooling curves failed to give satisfactory records of the heat changes at the transition point and even at the solidification point due to the tendency for supercooling † and the inefficiency of the stirring, heating curves gave conclusive results. In Fig. I, which represents a typical heating curve, the temperature is plotted in microvolts (without calibration correction), since the corresponding unit in degrees is an inconvenient figure, 0·0193° C. For the sake of clarity the corrected temperatures in degrees Centigrade are also given.



FIG. I.—Heating curve for *para*-methoxycinnamic acid. The dotted line represents the temperature of the sample ; the full line, that of the surroundings.

This curve shows definitely that the sample used was very pure,[9] that there are two similar heat changes, and that each takes place at constant temperature. Thus the upper arrest (the temperature at which the turbid liquid crystals change to the clear amorphous liquid) corresponds to an actual transition point involving a latent heat, just as in

* For the description of the apparatus, the interpretation of the curves and their use as a criterion of purity see the first paper of this series : Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551, 1933. For the method of calibrating the thermocouple see Skau and Saxton, *J. Am. Chem. Soc.*, **50**, 2693, 1928.

† It was possible to supercool the liquid to a temperature considerably below the solidification point without the appearance of the liquid crystals.

[7] Andrews, Kohman and Johnston, *J. Physic. Chem.*, **29**, 914, 1925 ; Skau and Saxton, *loc. cit. ;* Steiner and Johnston, *J. Physic. Chem.*, **32**, 912, 1928.

[8] Perkin and Hallworth, *J. Chem. Soc.*, **126**, 1693, 1924 ; Ingold and Shopper, *J. Chem. Soc.*, **132**, 449, 1929.

[9] Skau, *loc. cit.* See also paper VI. of this series, to appear soon in *J. Physic. Chem.*

the case of a melting-point, rather than, for example, to a point at which an emulsion forms [1] due to the separation of two non-miscible liquid layers. The values obtained for the freezing-point and the clarification point are 172·1° C. and 187·3° C. respectively.

The relative magnitude of the heats absorbed in the change from the solid-crystalline to the liquid-crystalline state and from the liquid-crystalline to the amorphous liquid state, respectively, is proportional to the areas corresponding to these heat changes.[7] By graphical measurement of these areas the ratio of the heat of fusion of the solid to the heat of fusion of the liquid crystals was found to be 7 to 1.

# THE SYSTEM BUTYRIC ACID—SODIUM HYDROXIDE—WATER.

## By C. R. BURY AND R. D. J. OWENS.

It is intended in this, and in succeeding papers, to give data for a series of three-component systems of the type $HX$—$MOH$—$H_2O$ (where $HX$ is a fatty acid and $M$ a metal) in order to trace the changes that occur as the number of carbon atoms in the fatty acid increases and as the nature of the metal is changed.

One system of this type—the system acetic acid—sodium hydroxide-water has been studied by Dunningham.[1] Our object in studying the system butyric acid—sodium hydroxide—water was as follows : there is a critical solution point in the two-component system butyric acid—water at — 3° C. [2, 3] and critical solution temperatures are usually raised by the addition of electrolytes. It was therefore hoped that two liquid phases would be encountered in the three-component system butyric acid—sodium hydroxide—water due to the salting-out effect of sodium butyrate on butyric acid and that this system would illustrate the transition between the acetic acid system studied by Dunningham and systems involving higher fatty acids which are not completely miscible with water. Unfortunately for this purpose, however, two liquid phases were not found.

## Experimental.

Butyric acid was purified by several fractional freezings, or by one distillation of a good commercial sample. The first method is much more laborious and appears only to remove water, which was unimportant for our purpose. Suitable quantities of carbonate—free alkali, butyric acid, and water were placed in resistant glass test-tubes which were shaken

[1] *J.C.S.*, 1912, **101**, 431.          [2] Faucon, *Ann. chim. physique*, **19**, 70, 1910.
[3] Timmermans, *Z. physik. Chem.*, **58**, 129, 1907.

in a thermostat at 25° C. for periods varying from a week to a month. The contents of the tubes were then filtered through a sintered glass filter, the operation being performed in the thermostat and in a carbon dioxide-free atmosphere. Solutions containing a large excess of acid were very viscous, and difficult to separate from the solid. The solution and moist solid were analysed ; excess acid or alkali being determined by titration, and total sodium by conversion to the chloride. All results quoted in the table are the mean of two concordant estimations. Analyses were found independent of the period of shaking. Traces of carbonate and of silica were found in some of the more strongly alkaline tubes, but we believe that these were insufficient to affect our results appreciably.

Analyses are expressed in terms of the three components sodium oxide ($Na_2O$), butyric anhydride ($(C_4H_7O)_2O$), and water : there are other possible choices of the substances to be regarded as the components of the system, but any choice other than the one adopted would necessitate the use of negative concentrations.

| Solution. | | Moist Solid. | | Solid Phase. |
|---|---|---|---|---|
| $Na_2O$. | $C_8H_{14}O_3$. | $Na_2O$. | $C_8H_{14}O_3$. | |
| 40·56 | — | — | — | NaOH, $H_2O$. |
| 40·62 | 0·77 | 43·80 | 6·38 | NaOH, $H_2O$ and $C_4H_7O_2Na$. |
| 40·61 | 0·80 | 38·75 | 13·20 | |
| 39·01 | 0·50 | — | — | |
| 33·88 | 0·76 | 32·39 | 21·98 | |
| 31·54 | 0·52 | — | — | |
| 29·05 | 0·58 | 29·03 | 8·43 | |
| 23·81 | 1·00 | 24·46 | 12·40 | |
| 22·18 | 1·18 | 23·16 | 11·66 | $C_4H_7O_2Na$. |
| 21·24 | 1·78 | 21·96 | 9·06 | |
| 20·38 | 3·09 | 21·28 | 11·39 | |
| 19·83 | 4·45 | — | — | |
| 19·29 | 6·50 | 20·19 | 13·31 | |
| 18·86 | 11·66 | 19·34 | 14·63 | |
| 18·36 | 12·74 | 19·19 | 19·63 | |
| 17·24 | 17·93 | 18·32 | 23·29 | |
| 16·89 | 20·70 | 18·12 | 26·48 | |
| 16·53 | 24·01 | 18·39 | 33·04 | |
| 15·90 | 27·22 | 16·90 | 30·80 | |
| 15·10 | 32·97 | 17·51 | 41·07 | $C_4H_7O_2Na$, $H_2O$. |
| 14·58 | 35·26 | — | — | |
| 14·31 | 37·77 | 15·63 | 40·93 | |
| 14·27 | 41·34 | 15·38 | 43·75 | |
| 14·19 | 43·55 | 15·15 | 45·44 | |
| 13·92 | 46·44 | 15·17 | 48·72 | |
| 13·82 | 49·76 | 14·82 | 51·05 | |
| 13·47 | 52·07 | 13·80 | 53·41 | |
| 13·50 | 53·35 | 14·02 | 55·26 | |
| 12·40 | 60·72 | 15·12 | 66·49 | |
| 12·04 | 66·48 | 13·50 | 68·98 | |
| 11·03 | 74·63 | 13·85 | 75·14 | $2C_4H_7O_2Na$, $C_4H_8O_2$. |
| 10·76 | 77·85 | 12·16 | 78·04 | |
| 10·59 | 79·92 | 13·11 | 79·30 | |
| 10·35 | 82·28 | 13·21 | 81·04 | |

## Discussion.

The results are illustrated in the figure, the usual triangular figure being employed ; many experimental points are omitted for the sake of clearness. Four solid phases—sodium hydroxide monohydrate

(NaOH, $H_2O$), anhydrous sodium butyrate ($C_4H_7O_2Na$), sodium bu-
tyrate monohydrate ($C_4H_7O_2Na$, $H_2O$), and acid sodium butyrate
($2C_4H_7O_2Na$, $C_4H_8O_2$),—are formed.  The system closely resembles the
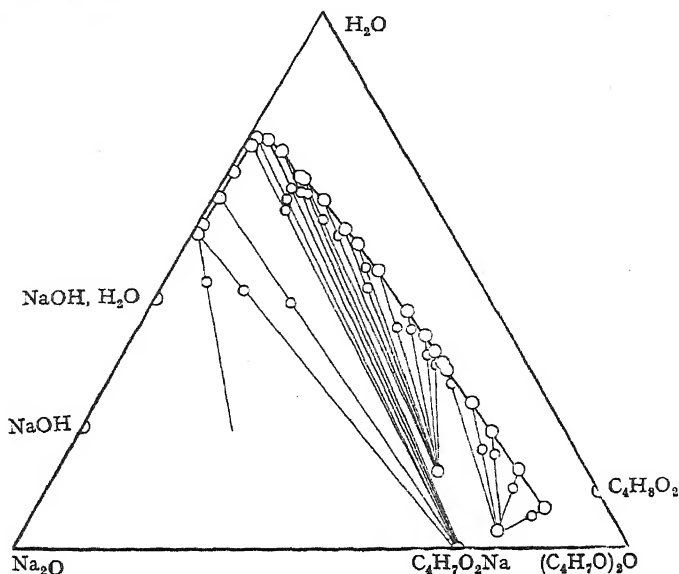


corresponding acetic acid system except that two acid salts are formed
in the latter system.   One noticeable feature of this system is that alkali
strongly represses the solubility of the neutral salt, while excess acid
increases it.

*Edward Davies Chemical Laboratories,*
*University College of Wales,*
*Aberystwyth.*

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# SUBSTITUTION BY FREE ATOMS AND WALDEN INVERSION. THE DECOMPOSITION AND RACEMISATION OF OPTICALLY ACTIVE SEC-BUTYL IODIDE IN THE GASEOUS STATE.

By R. A. OGG, JR.,[1] AND M. POLANYI.

In a previous communication [2] examples have been given of the
racemisation of simple optically active alkyl halides by the corresponding
halide ions in acetone solution.   Similar reactions are known for halo-
genated succinic acids in aqueous solution.[3]   These are examples of the

[1] International Research Fellow in Chemistry.
[2] E. Bergmann, M. Polanyi and A. Szabo, *Z. physik. Chem.*, **20B**, 161, 1933;
A. Szabo, *Dissertation*, Berlin, 1933.

general rule which has been first noticed by B. Holmberg,[3] and has been given a theoretical foundation by N. Meer and M. Polanyi;[4] that replacement in an organic compound of a negative substituent by a negative ion leads to optical inversion. It has been pointed out by the latter authors,[5] that in such reactions the negative ion approaches the positive end of the carbon-halogen (or other negative substituent) dipole, and hence that optical inversion necessarily results.

It is of interest to consider substitution by a free atom rather than by a negative ion. In this case no appreciable electrostatic forces influence the approach of the uncharged atom. However, in the reaction of a free monovalent atom with a diatomic molecule (consisting of two monovalent atoms) it has been shown [6] that the activation energy resulting from interchange forces is a minimum when the three atomic nuclei lie on a straight line. While the situation is considerably more complicated in the case of a monovalent atom attacking a hydrocarbon radical bound to another monovalent atom, it nevertheless appears that essentially the same general principles must apply to the latter case as to the former, and that the activation energy is a minimum when the approach of the atom is along the axis of the linkage attached. Hence optical inversion is to be expected in substitution by a free atom as well as in that by a negative ion.

Heretofore there has been no experimental evidence in support of this conclusion, and the object of the present investigation was to supply such evidence. The possible scope of such an investigation is limited by the tendency of most free atoms to effect rather deep-seated changes in organic molecules, which would mask the reaction sought. Thus gaseous hydrogen atoms cause rupture of carbon-hydrogen, and probably also carbon-carbon bonds. Chlorine and bromine atoms induce halogenation through reaction chains involving free hydrocarbon radicals. Iodine atoms would appear to be the only ones sufficiently inert to cause substitution without serious side reactions.

From the above conclusion it is to be expected that free iodine atoms would effect in optically active alkyl iodides a substitution accompanied by optical inversion—a reaction which by its reversibility must lead to the racemisation of the iodide,

$$I \; + \; \underset{\substack{| \\ R_3 \\ d(\text{or } l)}}{\overset{\substack{R_1 \;\; R_2 \\ \diagdown \diagup}}{C}} - I \quad \longrightarrow \quad I - \underset{\substack{| \\ R_3 \\ l(\text{or } d)}}{\overset{\substack{R_1 \;\; R_2 \\ \diagdown \diagup}}{C}} \; + \; I$$

Experiments were therefore undertaken with the object of establishing the occurrence of a reaction of this sort, preferably in the gas phase, and of studying its kinetics.

### Preliminary Observations.

The iodide chosen for these experiments was methyl ethyl iodo-methane *i.e.*, sec-butyl iodide, as being the simplest and presumably most stable

[3] B. Holmberg, *J. prakt. Chem.* (2), **88**, 576, 1913 ; A. R. Olson and F. A. Long, *J. Am. Chem. Soc.*, **56**, 1294, 1934.
[4] *Z. physik. Chem.*, 19B, 164, 1932.
[5] See also M. Polanyi, *Proc. Roy. Soc.*
[6] F. London, *Sommerfeld Festband*, 1928, p. 104. H. Eyring and M. Polanyi, *Z. physik. Chem.*, 12B, 279, 1931.

optically active alkyl iodide. Tests of the stability of this substance in the gas phase were made by heating in an air bath sealed bulbs (of German soda glass) containing the pure vapour at pressures around a few hundred mm. Hg, and judging the extent of decomposition by the quantity of iodine produced. At temperatures up to about 200° C. the iodide was practically unaffected, only a faint coloration appearing after several hours. Above 200° C. the decomposition was noticeable, although not rapid below about 270° C. This decomposition appeared to produce only iodine and low boiling, inflammable hydrocarbons, giving a strong test for unsaturation. No hydrogen iodide was detected. These facts, coupled with the nearly 50 per cent. increase of pressure on total decomposition (*vide infra*), suggest that the decomposition yields chiefly butane and butylene.

$$sec-C_4H_9I \longrightarrow \tfrac{1}{2}C_4H_{10} + \tfrac{1}{2}C_4H_8 + \tfrac{1}{2}I_2.$$
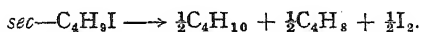
This is entirely analogous to the decomposition of the closely related *iso*-propyl iodide, observed by Glass and Hinshelwood.[7]

Heating of the iodide vapour in bulbs containing iodine caused no appreciable decomposition at temperatures below 200° C.

The above experiments were made with the racemic iodide. The rotation of the optically active substance was found to be practically unaffected by heating the pure vapour below 200° C. However, if the vapour was heated with small amounts of iodine (10-50 mm. Hg pressure), the iodide after recovery and purification was found to have undergone a considerable loss of optical activity, being completely inactive after extended heating. This racemising action was found to be moderately rapid at temperatures as low as 150° C.

It at first appeared that this was the reaction sought. However, a brief study of its kinetics at 150-180° indicated the reaction velocity to have an abnormally small temperature coefficient, while a comparison of reaction rates in bulbs of different surface-volume ratios (produced by packing with bits of broken tubing) indicated that the reaction is almost completely heterogeneous at these temperatures.

This racemisation of active *sec*-butyl iodide by iodine at a glass surface is not without interest (see the discussion), but is hardly as satisfactory a proof of the original thesis as would be the homogeneous gas reaction, and hence attempts were continued to find the latter. Since the heterogeneous reaction has a very small temperature coefficient (corresponding to an activation energy of some 8000 gram calories per mol.) while a much larger one is to be expected for the homogeneous reaction, it appeared that the latter would predominate at higher temperatures. However, the racemisation in the presence of added iodine was found to be still partially heterogeneous at 200-210° C., while at higher temperatures it was too rapid to allow of accurate measurement of the rate.

To circumvent this difficulty, recourse was had to a study of the racemisation of active *sec*-butyl iodide caused by the iodine resulting from its own partial decomposition at still higher temperatures. At 240-280° the racemisation of the *undecomposed* iodide was found to be very extensive, even when the decomposition had proceeded to the extent of only a few per cent. of the original material. The homogeneity of the reaction under these conditions was tested by heating simultaneously in an air bath bulbs containing equal *concentrations* of the vapour of pure active *sec*-butyl iodide. The surface-volume ratio of the bulbs differed ten-fold as a result of packing one of them with bits of broken tubing. After heating for a suitable period, the bulbs were removed and cooled simultaneously. The undecomposed fraction of iodide from each was then recovered, and after purification as described below, its optical rotation was determined.

In several sets of experiments made at approximately 240° C. and at pressures of *sec*-butyl iodide vapour of about 200 mm. Hg the rotations

[7] J. V. S. Glass and C. N. Hinshelwood, *J. Chem. Soc.*, 1929, 1804.

of the iodide from the packed and empty bulbs were found to be identical within the experimental error. This is a satisfactory proof of the homogeneity of the racemisation under these conditions. Since the subsequent kinetic measurements were made in a reaction vessel of a glass identical with that used in these experiments, in the temperature range 238-276° C. and at pressures of *sec*-butyl iodide vapour of 100-200 mm. Hg, it seems reasonable to infer that they deal with an essentially homogeneous reaction.

The homogeneity of the racemisation process is itself a strong argument for the homogeneity of the decomposition which produces the necessary iodine. This was further verified by direct measurement of the iodine produced, the ratio of iodine to *sec*-butyl iodide proving to be the same for the packed and unpacked reaction vessels.

To remove any possible doubt that the loss in optical activity by active *sec*-butyl iodide under the above treatment is really the result of a racemisation and not of some chemical change, a few grams of the pure racemic liquid was sealed up in a large evacuated glass bulb, which was then heated for some hours at around 240°—a procedure sufficient to cause complete loss of optical activity by the active iodide. The liquid was then collected and purified of iodine. The boiling-point and index of refraction of the purified liquid proved to be identical with those for pure *sec*-butyl iodide, indicating that no chemical change or molecular rearrangement had taken place.

The occurrence of the decomposition of *sec*-butyl iodide and of the racemisation of active *sec*-butyl iodide as homogeneous gas phase reactions under the above conditions having been established, the quantitative study of the kinetics of these two processes was undertaken, as described below.

## Experimental Details of Reaction Rate Measurements.

**Preparation of Materials.**—The racemic *sec*-butyl alcohol used was a British Drug Houses product, and was carefully fractionated before use, the middle fraction boiling at 99·5-100° C. It was separated into its optical antipodes by the method of Pickard and Kenyon.[8] Since optical purity was unessential, the brucine salt was divided into only three crystal fractions.

Racemic *sec*-butyl iodide was prepared according to the method of Norris,[9] by distilling racemic *sec*-butyl alcohol with three molar equivalents of concentrated hydriodic acid. It was washed with dilute alkali and water, and then dried and distilled, yielding a colourless liquid B.P. 117.5° C.

*d-Sec*-butyl iodide was prepared in accordance with the directions of Szabo[10] by saturating *l-sec*-butyl alcohol with dry hydrogen iodide at 0° C., and then heating it in a sealed tube for one-half hour at 50° C. It was purified in the same manner as the racemic substance. The product used in this investigation boiled at 117·5° C., and had a value of $[\alpha]_D^{20°}$ in acetone solutions of + 6·32°.

Both the racemic and active iodides were stored in the dark when not in use, and remained colourless over the period required for the investigation.

**Apparatus and Procedure.**—Since for practical reasons it was not feasible to determine the rotation of the active *sec*-butyl iodide in the gaseous state, the rate of racemisation was found from successive experiments made with separate samples. Measured quantities of the substance were heated in the vapour state for ascertained time intervals, and after condensation and purification the specific rotations were determined in acetone solution. In these experiments the iodine formed by decomposition was also collected and quantitatively estimated by chemical analysis.

[8] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45, 1911.
[9] J. F. Norris, *Am. Chem. Journ.*, **38**, 627, 1907.
[10] A. Szabo, *Dissertation*, Berlin, 1933.

The decomposition velocity of the racemic *sec*-butyl iodide was measured by following the pressure change attending the reaction at constant volume.

The essential details of the apparatus employed are shown in Fig. 1. The construction was of German soda glass throughout. The reaction vessel was a cylindrical bulb of some 400 cm.$^3$ capacity, surrounded by a mantle in which the vapour of a liquid boiling under atmospheric pressure was refluxed. A constant temperature was thus assured. The liquids chiefly used were acenaphthene (B.P. 277° C.), diphenyl (255°) and *p*-nitro-toluene (238°). The data in the Landolt-Börnstein Tabellen were used to correct the boiling-points for differences of barometric pressure.

Gas pressure in the reaction cell was measured with a mercury mano-meter, using an intervening glass " click gauge " [11] as a null instrument. The glass tubing joining the cell to the click gauge and to the tap connecting with the remaining system was of very small diameter to reduce the outside volume. This tubing, as well as tap C and the large tubing sur-rounding the clicker, were all wound with heating wire and lagged with asbestos, and hence could be maintained at some 150° C. to prevent con-densation of iodine and *sec*-butyl iodide. The small bare side arm B,
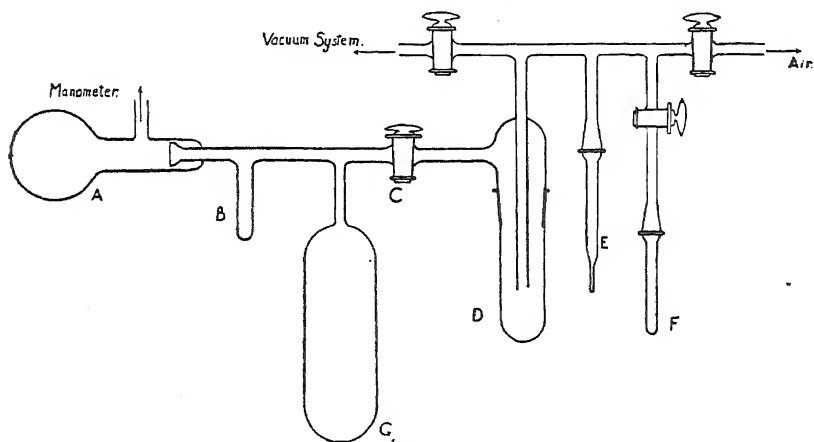


FIG. 1.

when not in use, was covered with a tiny auxiliary heater to prevent condensation. The tap C was lubricated with a hard vacuum wax, found to have approximately the correct consistency at the above temperature. This wax appeared also to be quite resistant to attack by iodine vapour.

The system could be evacuated through a liquid air trap with a three-stage mercury diffusion pump to some $10^{-5}$ mm. Hg.

The procedure of a typical experiment dealing with the racemisation follows. The appropriate quantity (generally 0·2-0·5 g.) of active *sec*-butyl iodide was introduced into F, and after evacuation of the system (the iodide being first cooled with solid carbon dioxide and acetone) was condensed in the small side arm B by cooling with solid carbon dioxide. Tap C was then closed, and the iodide was rapidly vaporised by flaming B, the stop-watch being started simultaneously. The pressure was then measured. After a suitable time interval the reaction was stopped by condensing the iodide in P. Both the vaporisation and condensation occupied less than five seconds —a correction that was usually negligible. Tap C was then opened, and the condensed iodide and iodine were allowed to distill at very low pressure into the trap D, cooled by solid carbon dioxide. Removal of the volatile

[11] J. A. Leermakers and H. Ramsperger, *J. Am. Chem. Soc.*, **54**, 1837, 1932.

hydrocarbons and transfer of the last trace of $I_2$ from the reaction vessel to D were effected by finally evacuating directly with the pump. Tap C was then closed, and after admitting air the bottom part of D was removed. A few drops of mercury were added to the condensed iodide and shaken, thereby absorbing the iodine and leaving the iodide colourless. The bottom half of D was then replaced, and after cooling of the iodide with solid carbon dioxide the system was again exhausted to a very low pressure. The purified *sec*-butyl iodide was then condensed in E, leaving mercury and mercury iodides in D. Air was again admitted, and E was removed. The sharp tip, previously file-scratched, was inserted into the neck of a 3 cm.³ volumetric flask and snapped off, allowing the *sec*-butyl iodide to run into the flask. By this procedure the loss of liquid was minimised. The flask plus iodide was then weighed, and after addition of acetone to the mark, the rotation of the resulting solution in a 20 cm. micropolarimeter tube was measured. The small bit of glass (from the tip of E) was extracted and weighed, and the corresponding correction applied to the weight of the iodide. The mercury and mercury iodides remaining in D were boiled with zinc dust and a small quantity of water for a few minutes, causing quantitative reduction to soluble zinc iodide and mercury. After filtration and washing of the residues the filtrate was analysed for iodide ion by titration with 0·02 N$AgNO_3$ solution, using $K_2CrO_4$ as an indicator.

The optical rotations were measured with a Hilger instrument, using a Pirani sodium lamp as a source of the D lines. Duplicate readings generally agreed to better than 0·01°, the difference never exceeding 0·02°. The actual rotations measured were generally 0·10°-1·00°. The probable error was thus usually only a few per cent.

The few experiments made on the racemisation in the presence of added iodine did not differ greatly in technique from the above. After the measurement of the pressure of *sec*-butyl iodide vapour the substance was condensed again in B with solid carbon dioxide. Tap C was then opened and iodine was allowed to sublime into B from D—a very slow process. C was then closed, and after vaporisation of the contents of B the total pressure was measured. The partial pressure of iodine vapour was thus determined by difference. The succeeding operations were identical with the above—only the analysis for $I_2$ being omitted.

The start of an experiment on the decomposition of racemic *sec*-butyl iodide was identical with that for the racemisation. However, the experiments were extended over much greater periods, and readings of the pressure were made at frequent intervals. Initial pressures were obtained by extrapolation. In several experiments the decomposition was allowed to proceed to completion in order to find the ratio of final to initial pressure. Experiments on the rate of decomposition in the presence of added iodine were carried out in the fashion described in the preceding paragraph, *i.e.*, the pressure of added $I_2$ vapour was determined by difference.

The accuracy of the experiments dealing with decomposition of the iodide is inferior to that of those on the racemisation. This is due in large part to the somewhat erratic behaviour of the heated soft glass click gauge (such gauges are most satisfactory when made of Pyrex glass and operated at room temperature), introducing considerable errors into the measurement of small pressure differences. Nevertheless, the accuracy was adequate to show clearly the general character of the decomposition.

## Experimental Results.

### The Heterogeneous Racemisation of Active *sec*-Butyl Iodide by Iodine.

Results of the few experiments made were best represented by the rate expression

$$-\frac{d\alpha}{dt} = k_1(I_2)^{\frac{1}{2}}\alpha, \qquad . \qquad . \qquad . \qquad . \quad (1)$$

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or rather by the integrated form

$$\ln\frac{\alpha_0}{\alpha_t} = k_1(I_2)^{\frac{1}{2}}t, \qquad . \qquad . \qquad . \qquad . \quad (2)$$

where $\alpha_0$ represents the initial specific rotation and $\alpha_t$ that after time $t$. Constants calculated on the basis of this equation are shown in Table I. The temperatures used were the boiling-points of bromobenzene and aniline.

TABLE I.—RATE OF HETEROGENEOUS RACEMISATION.

| $T.$ °C. | $P_{BuI}.$ mm. Hg. | $P_{I_2}.$ mm. Hg. | $t.$ secs. | $[\alpha_0]_D^{20°}.$ o. | $[\alpha_t]_D^{20°}.$ o. | $k_1 \times 10^7$ $\left(\frac{\text{mol.}}{\text{cc.}}\right)^{-\frac{1}{2}}$ sec.$^{-1}$. |
|---|---|---|---|---|---|---|
| 184 | 82·3 | 23·8 | 1,500 | + 7·55 | + 6·40 | 1·210 |
|  | 101·0 | 11·5 | 3,200 |  | + 6·00 | 1·135 |
| 156 | 83·1 | 29·0 | 9,600 |  | + 3·80 | 0·688 |
|  | 91·5 | 10·4 | 19,200 |  | + 3·58 | 0·624 |

The agreement is seen to be satisfactory. The energy of activation, calculated from the average values at the two temperatures, is found to be some 8000 gram calories per mole. These figures are not of great accuracy, but suffice to show the salient characteristics of the heterogeneous reaction.

### The Homogeneous Racemisation of Active *sec*-Butyl Iodide.

The loss of optical activity on heating the pure substance in the vapour state was found to obey the expression

$$\ln\frac{\alpha_0}{\alpha_t} = k_2(C_4H_9I)^{\frac{1}{2}}t^3 \qquad . \qquad . \qquad . \qquad . \quad (3)$$

The rate of formation of iodine in these experiments (determined by chemical analysis) was given essentially by the rate expression

$$\frac{d(I_2)}{dt} = k_3(C_4H_9I) \qquad . \qquad . \qquad . \qquad . \quad (4)$$

used in the integrated form

$$(I_2)_t = k_3(C_4H_9I)t. \qquad . \qquad . \qquad . \qquad . \quad (5)$$

These facts indicate that the true rate expression for the racemisation of the active *sec*-butyl iodide by iodine is

$$-\frac{d\alpha}{dt} = k_4(I_2)^{\frac{1}{2}}\alpha \qquad . \qquad . \qquad . \qquad . \quad (6)$$

which in integrated form is

$$\ln\frac{\alpha_0}{\alpha_t} = k_4(I_2)^{\frac{1}{2}}t. \qquad . \qquad . \qquad . \qquad . \quad (7)$$

That this is the correct expression follows from the fact that the experimentally observed equation (3) can be derived from (5) and (6).

From (5), at time $t$,

$$(I_2)^{\frac{1}{2}} = k_3^{\frac{1}{2}}(C_4H_9I)^{\frac{1}{2}}t^{\frac{1}{2}}.$$

Substituting in (6)

$$-\frac{d\alpha}{dt} = k_4 k_3^{\frac{1}{2}}(C_4H_9I)^{\frac{1}{2}}t^{\frac{1}{2}}\alpha.$$

Integrating and evaluating the integration constant

$$\ln\frac{\alpha_0}{\alpha_t} = \frac{2}{3} k_4 k_3^{\frac{1}{2}}(C_4H_9I)^{\frac{1}{2}}t^{\frac{3}{2}}. \qquad . \qquad . \qquad . \qquad . \quad (9)$$

This is seen to be identical with equation (3). Hence the desired rate constant is derived from the observed ones by the expression

$$k_4 = \frac{3}{2}\frac{k_2}{k_3^{\frac{1}{2}}}. \qquad\qquad\qquad (10)$$

In Table II. are given the data for the experiments on the racemisation, together with the observed values of $k_2$ and $k_3$, and the values of $k_4$, calculated from equation (10). In each of these experiments the fraction of the sec-butyl iodide decomposed was so small that $(C_4H_9I)$ could be considered constant without introducing an appreciable error. In three of the experiments at the lowest temperature ($238°$ C.) mishaps prevented the determination of the amount of iodine formed, and hence the corresponding

TABLE II.

| T. °C. | $P_{BuI}$. mm. Hg. | t. secs. | $[\alpha_0]_D^{20°}$. o. | $[\alpha_t]_D^{20°}$. o. | Vol. Cell. cc. | Vol. 0·02N. AgNO₃. cc. | $k_2 \times 10^2$. $\left(\frac{mol.}{cc.}\right)^{-\frac{1}{2}}$ sec.$^{-\frac{3}{2}}$. | $k_3 \times 10^6$. sec.$^{-1}$. | $k_4$. $\left(\frac{mol.}{cc.}\right)^{-\frac{1}{2}}$ sec.$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 276·0 | 113·6 | 360 | + 6·32 | + 2·68 | 400·0 | 5·480 | 69·0 | 115·0 | 9·65 |
| | 113·3 | 360 | | 2·31 | | 6·840 | 81·0 | 148·7 | 9·95 |
| | 109·3 | 540 | | 1·19 | | 9·500 | 74·6 | 138·5 | 9·50 |
| | 117·5 | 90 | | 5·60 | | 1·848 | 76·3 | 150·4 | 9·34 |
| | 113·3 | 180 | | 4·55 | | 2·900 | 74·9 | 122·2 | 10·17 |
| | 189·5 | 180 | | 4·02 | | 4·810 | 79·6 | 121·1 | 10·84 |
| | 188·9 | 360 | | 1·90 | | 9·800 | 75·2 | 123·8 | 10·14 |
| | | | | | | | Av. 75·9 | 132·0 | 9·94 |
| 255·5 | 169·5 | 720 | + 6·32 | + 3·87 | 400·0 | 4·200 | 11·20 | 28·4 | 3·15 |
| | 189·1 | 1080 | | 2·28 | | 7·585 | 11·99 | 30·7 | 3·24 |
| | 167·5 | 360 | | 5·22 | | 2·080 | 12·37 | 28·6 | 3·46 |
| | 228·2 | 720 | | 3·60 | | 6·310 | 11·10 | 31·8 | 2·95 |
| | 96·8 | 720 | | 4·31 | | 2·520 | 11·61 | 28·9 | 3·24 |
| | 103·5 | 1080 | | 3·03 | | 4·418 | 11·72 | 27·7 | 3·34 |
| | 103·5 | 360 | | 5·46 | | 1·420 | 12·06 | 31·4 | 3·22 |
| | 105·1 | 1800 | | 1·42 | | 7·450 | 10·97 | 32·4 | 2·89 |
| | | | | | | | Av. 11·63 | 30·6 | 3·18 |
| 238·0 | 100·8 | 7800 | + 6·32 | + 0·42 | 380·0 | * | 2·22 | * | |
| | 101·9 | 1200 | | 5·34 | | 1·250 | 2·28 | 8·60 | |
| | 112·7 | 3600 | | 2·64 | | 3·970 | 2·15 | 8·25 | |
| | 111·5 | 2400 | | 3·84 | | * | 2·27 | * | |
| | 182·0 | 1200 | | 5·14 | | 2·250 | 2·09 | 8·70 | |
| | 171·2 | 2400 | | 3·58 | | * | 2·09 | * | |
| | 206·8 | 3600 | | 2·11 | | 7·410 | 1·99 | 8·35 | |
| | | | | | | | Av. 2·16 | 8·48 | 1·112 |

values of $k_3$ are missing from the table (the omissions are marked by asterisks). Therefore the average value of $k_4$ at this temperature is calculated from the average values of $k_2$ and $k_3$. This procedure is justified by the fact that at the other two temperatures there is a close agreement between the values of $k_4$ obtained by averaging the individual quantities and those calculated from the averages of $k_2$ and $k_3$.

It is seen that the random fluctuations around the mean values of the constants are some ± 5 per cent. Differences of this magnitude are within the experimental error. The range of conditions is fairly wide, and hence the essential validity of the rate expressions (3), (4) and (6) is confirmed.

The activation energies $Q_2$, $Q_3$ and $Q_4$, corresponding respectively to the rate constants $k_2$, $k_3$ and $k_4$ are calculated by the usual Arrhenius equation for the different temperature intervals employed. The average

values Table (II.) of the constants at the respective temperatures are used for these calculations. The results are given in Table III.

The values corresponding to the different intervals are in satisfactory agreement, indicating that the Arrhenius equation is accurately obeyed. The activation energies which we shall select as the most probable are those for the entire temperature range, *i.e.*, those given in the first row of Table III. These are probably correct to within 1000 cals./mol. It should

TABLE III.—ACTIVATION ENERGIES.

| Temperature. Interval °C. | $Q_2$. Cals./mol. | $Q_3$. Cals./mol. | $Q_4$. Cals./mol. |
|---|---|---|---|
| 276·0-238·0° | 52,280 | 40,320 | 32,180 |
| 276·0-255·5° | 52,720 | 41,090 | 32,040 |
| 255·5-238·0° | 51,780 | 39,480 | 32,320 |

be noted that from equation (10) a relation must obtain between $Q_2$, $Q_3$ and $Q_4$.

$$Q_2 = \tfrac{1}{2}Q_3 + Q_4.$$

This is verified by the values given, any slight differences arising from the methods of averaging the constants.

### The Homogeneous Decomposition of Racemic *sec*-Butyl Iodide.

This reaction was studied in the same temperature range as the above racemisation. In this range the ratio of final to initial pressure was found to be 1·47, practically independent of temperature and initial pressure of the iodide. Hence at a total pressure, $P$, the partial pressure of undecomposed iodide was given by the expression

$$P_{\mathrm{BuI}} = \frac{1\cdot47\,P_0 - P}{0\cdot47},$$

where $P_0$ represents the initial pressure of the pure iodide. The decomposition was found to be autocatalytic, and experiments with added iodine showed that it was this substance which produced acceleration of the reaction.

The experimental results on the rate were represented best by the kinetic expression

$$- \frac{d(C_4H_9I)}{dt} = k_5(C_4H_9I) + k_6(I_2)^{\frac{1}{2}}(C_4H_9I). \qquad . \qquad . \quad (11)$$

A similar expression was found by Arnold and Kistiakowsky,[12] to obtain for the decomposition of ethylene iodide. Equation (11) was tested by plotting the quantity

$$\frac{\Delta(C_4H_9I)}{\Delta t} \cdot \frac{1}{(C_4H_9I)_{Av.}}$$

(for successive short time intervals) against $(I_2)^{\frac{1}{2}}$. The result should be a straight line whose intercept is $k_5$ and whose slope is $k_6$. Fig. 2 represents such an analysis of the experimental results. The three different lines in Fig. 2 refer to sets of experiments at 276°, 254° and 238° C. respectively. The range of initial pressures of *sec*-butyl iodide was 100-250 mm. Hg. In computing iodine concentrations it was assumed that 2 molecules of the iodide decomposing yield 1 molecule of iodine. On the whole the agreement of the results with equation (11) is fairly satisfactory. The scattering of the experimental points is attributed to errors in pressure measurement resulting from the erratic behaviour of the click gauge.

In Table IV. are listed the values of the constants $k_5$ and $k_6$ obtained

[12] L. B. Arnold, Jr., and G. B. Kistiakowsky, *J. Chem. Physics*, **1**, 166, 1933.

TABLE IV.—RATE CONSTANTS.        TABLE V.—ACTIVATION ENERGIES.

| $T.$ °C. | $k_5 \times 10^5.$ sec.$^{-1}$ | $k_6 \times 10^2.$ $\left(\frac{\text{mol.}}{\text{cc.}}\right)^{-\frac{1}{2}}$sec.$^{-1}$ | Temperature. Interval °C. | $Q_5.$ Cals./Mol | $Q_6.$ Cals./Mol |
|---|---|---|---|---|---|
| | | | 276·0–238·0 | 39,420 | 35,220 |
| 276·0 | 19·00 | 26·4 | 276·0–254·0 | 40,800 | 36,040 |
| 254·0 | 4·00 | 6·67 | 254·0–238·0 | 37,600 | 34,190 |
| 238·0 | 1·30 | 2·40 | | | |

from Fig. 2, and in Table V. the corresponding activation energies $Q_5$ and $Q_6$ for the different temperature intervals.

From Table V. it is seen that the Arrhenius equation is obeyed. For the most probable values of $Q_5$ and $Q_6$ we shall choose those referring to the extremes of temperature, *i.e.*, those in the first row of Table V.

It is of interest to compare the above results with those on the racemisation. The rate constant $k_4$ (Table II.) relates to a racemisation of the iodide by iodine, $k_6$ to a decomposition. For both reactions the rate is proportional to $(I_2)^{\frac{1}{2}}$. In this temperature range $k_4$ is seen to be some forty times larger than $k_6$. This large difference allows the racemisation to be studied essentially separate from the decomposition. $Q_6$ is also seen to be some 3000 calories larger than $Q_4$. There is thus no doubt that the racemisation
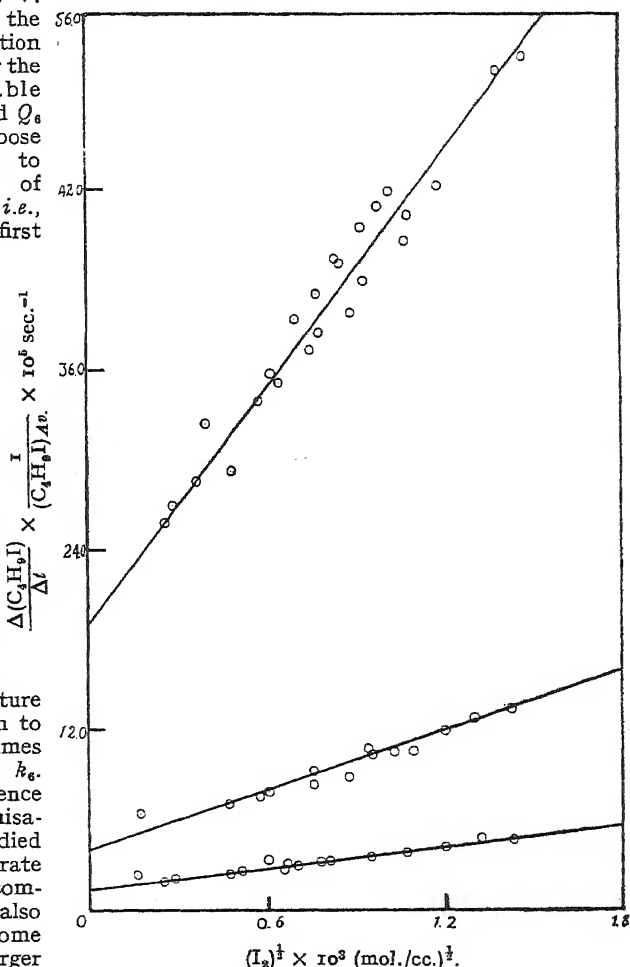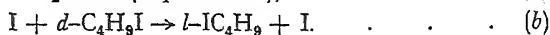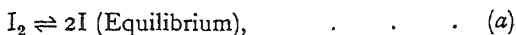


FIG. 2.—Decomposition of *sec*-butyl iodide.
The three lines refer to experiments at 276°, 254° and 238° C.

and decomposition processes are entirely separate.

17 *

$k_5$ measures the rate of decomposition of *sec*-butyl iodide by a mono-molecular reaction at a vanishing concentration of iodine. The rate of production of iodine should then be $\frac{1}{2}k_5$. Now $k_3$ (Table II.) gives the rate of formation of $I_2$ (as determined by chemical analysis) in the early stages of decomposition. The values of $k_3$ are seen to be in essential agreement with those of $\frac{1}{2}k_5$ at corresponding temperatures, but are some 30 per cent. larger than the latter. This difference is of the direction and magnitude to be expected, since in the experiments used to determine $k_3$ the average iodine concentration was of an appreciable finite value, and hence an increase in rate due to the sensitised decomposition ($k_6$) resulted. Likewise, $Q_3$ (Table III.) is slightly higher than $Q_5$, but essentially of the same size. This agreement between entirely independent methods of measuring the decomposition velocity gives considerable confidence in their correctness.

## Discussion.

The rate expression for the racemisation of active *sec*-butyl iodide by iodine (equation (6)) is explained by the following mechanism :

$$I_2 \rightleftharpoons 2I \text{ (Equilibrium)}, \qquad . \qquad . \qquad . \qquad (a)$$

$$I + d\text{-}C_4H_9I \rightarrow l\text{-}IC_4H_9 + I. \qquad . \qquad . \qquad . \qquad (b)$$

Reaction ($b$) is seen to be an example of the optical inversion predicted in the first section.

It will be observed that each *sec*-butyl iodide molecule undergoing reaction ($b$) leads to the formation of a *pair* of racemic molecules, and hence that the rate of racemisation is just twice the rate of ($b$). If the rate of ($b$) is denoted by $k_b$ and the dissociation constant of iodine as $K_{I_2}$ then the relation to the observed rate constant $k_4$ (equation (6) and Table II.) is

$$k_b = \frac{k_4}{2K_{I_2}^{\frac{1}{2}}}$$

Likewise, if the energy of activation of ($b$) is $Q_b$ and the heat of dissociation of iodine $H_{I_2}$, then

$$Q_b = Q_4 - \tfrac{1}{2}H_{I_2}.$$

The dissociation constants and heat of dissociation of iodine may be calculated from the equation of Boden-stein and Starck.[13] In the temperature range covered in these experiments the mean value of $H_{I_2}$ is 36,800 cals./mol. The most probable value for $Q_4$ (Table III.) is 32,180 cals./mol. Therefore the value of $Q_b$ is 13,780 cals./mol. In Table VI. are given the values of $k_4$, $K_I$ and the calculated values of $k_b$ at the various temperatures.

### TABLE VI.

RATE OF OPTICAL INVERSION BY IODINE ATOMS.

| $T.$ °C. | $K_{I_2}$. mol./cc. | $k_4$. (mol./cc.)$^{-\frac{1}{2}}$ sec$^{-1}$. | $k_b \times 10^{-7}$ (mol./cc.)$^{-1}$ sec.$^{-1}$. |
|---|---|---|---|
| 276·0 | 15·60 | 9·94 | 3·98 |
| 255·5 | 4·36 | 3·18 | 2·40 |
| 238·0 | 1·368 | 1·112 | 1·50 |

The energy of activation, or rather critical increment, calculated from the values of $k_b$ in Table VI., is some 14,300 cals./mol. This is, of course, equal to $Q_b + \frac{1}{2}RT$, a relation seen to be numerically satisfied by the

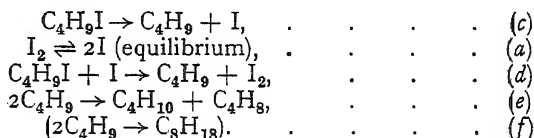[13] M. Bodenstein and H. Starck, *Z. Electrochem.*, **16**, 961, 1910.

above value of 13,780 cals./mol. for $Q_b$. In this temperature range the value of $k_b$ may be expressed as $5 \cdot 00 \times 10^{11} T^{\frac{1}{2}} e - \dfrac{13,780}{RT} \left(\dfrac{\text{mol.}}{\text{cc.}}\right)^{-1} \text{sec}^{-1}$.

Therefore, the rate of collisions between iodine atoms and *sec*-butyl iodide molecules effective in causing reaction (b) is given by

$$5 \cdot 00 \times 10^{11} T^{\frac{1}{2}} \left(\frac{\text{mol.}}{\text{cc.}}\right)^{-1} \text{sec.}^{-1}.$$

This corresponds to an effective collision diameter of $1 \cdot 56 \times 10^{-8}$ cm. If the " true collision diameter " is assumed to be some $5 \times 10^{-8}$ cm., this corresponds to a steric factor of approximately $0 \cdot 1$. Hence, the agreement of the rate with kinetic theory is entirely satisfactory, and in fact rather fortuitous, since there is some uncertainty in the activation energy.

But little can be said concerning the racemisation of *sec*-butyl iodide by iodine at a glass surface. The fair agreement of the experiments with equation (1) suggests that this is also an atomic exchange reaction, the iodine atoms and iodide molecules being absorbed on the glass surface. The smallness of the heat of activation (8000 cals./mol.) suggests that the heat of dissociation of iodine molecules on the surface is extremely small, and also that the optical inversion is easier than in the gas phase. this could well be due to a weakening of the carbon-iodine linkage by adsorption on the glass surface.

The rate expression for the decomposition of *sec*-butyl iodide (equation (11)) is explained by the mechanism

$$\begin{array}{llll} C_4H_9I \rightarrow C_4H_9 + I, & . & . & . & (c) \\ I_2 \rightleftharpoons 2I \text{ (equilibrium)}, & . & . & . & (a) \\ C_4H_9I + I \rightarrow C_4H_9 + I_2, & . & . & . & (d) \\ 2C_4H_9 \rightarrow C_4H_{10} + C_4H_8, & . & . & . & (e) \\ (2C_4H_9 \rightarrow C_8H_{18}). & . & . & . & (f) \end{array}$$

The rate controlling steps are the concurrent reactions (c) and (d). The rate of (c) is given by the constant $k_5$ (equation (11)). The overall rate of (a) followed by (d) is given by $k_8$. The secondary reactions (e) and (f) account for the products of decomposition. Reaction (e) is certainly the predominating step, but the fact that the final pressure increase is not quite 50 per cent. suggests the possibility of (f).

Reaction (c) is analogous to that found for the dissociation of primary aliphatic iodides,[14] methyl iodide for example. However, an important difference is to be noticed. In the dissociation of methyl iodide the reverse reaction (recombination of methyl radicals with iodine atoms) plays an important rôle, while it is apparently negligible here. Further, with methyl radicals the reaction analogous to the reverse of (d) is important, and again appears to play no significant rôle here. That the reverse of (c) and (d) are not important follows from the fact that iodine does not retard these processes. Also, were the reverse of (d) important, such a mechanism would cause a racemisation of the active iodide, since the free hydrocarbon radicals would most probably be racemised very rapidly. The above experiments on the racemisation show no evidence that such a reaction occurs. This difference in behaviour between methyl iodide and *sec*-butyl iodide may be explained by assuming that in the case of methyl radicals the reactions analogous to (e) and (f) are very much slower than with *sec*-butyl radicals.

[14] R. A. Ogg, Jr., *J. Am. Chem. Soc.*, **56**, 526, 1934.

The activation energy of $(c)$ is given by $Q_5$, whose probable value is some 39,420 cals./mol. (Table V.). Since the corresponding activation energy for the dissociation of primary aliphatic iodides is 43,000 cals./mol.,[14] it appears that the secondary carbon-iodine linkage is correspondingly weaker than is the primary linkage. In this temperature range the value of $k_5$ may be expressed as $8 \cdot 9 \times 10^{11} e^{\dfrac{-39,420}{RT}}$ sec.$^{-1}$. The temperature independent factor is of similar magnitude to those for the unimolecular decomposition of primary iodides.[14]

The constant $k_d$ for the rate of reaction $(d)$ is related to $k_6$ by the expression

$$k_d = \frac{k_6}{K_{I_2}^{\frac{1}{2}}}$$

while $Q_d = Q_6 - \frac{1}{2}H_{I_2}$, exactly as for reaction $(b)$. Hence

$$Q_d = 35,220 - 18,400 = 16,820 \text{ cals./mol.}$$

In Table VII. are given the calculated values of $k_d$ at the various temperatures. The calculations are exactly as for $k_b$ (Table VI.).

In the given temperature range the value of $k_d$ may be expressed as $4 \cdot 25 \times 10'' T^{\frac{1}{2}} e^{-\dfrac{16,820}{RT}}$ (mol./cc.)$^{-1}$ sec.$^{-1}$. This corresponds to an effective collision diameter of $1 \cdot 38 \times 10^{-8}$ cm., practically identical with that found for reaction $(b)$. Thus the reactions $(b)$ and $(d)$ apparently have essentially the same " steric factor," and the difference in their rates is due only to the difference of activation energies.

TABLE VII.

RATE OF DECOMPOSITION BY IODINE ATOMS.

| $T.$ °C. | $K_{I_2} \times 10^{15}$. Mol./cc. | $k_6 \times 10^2$. (mol./cc.)$^{-\frac{1}{2}}$ sec.$^{-1}$. | $k_d \times 10^{-5}$. (mol./cc.)$^{-1}$ sec.$^{-1}$. |
|---|---|---|---|
| 276·0 | 15·60 | 26·4 | 21·2 |
| 254·0 | 4·01 | 6·67 | 10·52 |
| 238·0 | 1·368 | 2·40 | 6·49 |

The reactions $(b)$ and $(d)$ represent two entirely different processes, involving the same reacting system—an iodine atom and a *sec*-butyl iodide molecule. The independence of the two processes is due to the difference of configuration which they require, as well as to a difference of activation energy. The discovery of such a case lends considerable weight to the conception that spatial relationships play a very important rôle in chemical reactions.

The heat effect in reaction $(d)$ should be the difference in dissociation energies of molecular iodine and of the carbon-iodine linkage in *sec*-butyl iodide. The activation energy $Q_5$ for the unimolecular dissociation of the latter is some 39,400 cals./mol. If we assume this to represent the actual heat of dissociation, then reaction $(d)$ is endothermic by some 2600 cals./mol. Therefore, if the activation energy of $(d)$ is 16,800 cals./mol. the activation energy of the reverse process (*i.e.* the reaction of the free *sec*-butyl radical with iodine) must be $16,800 - 2600 = 14,200$ cals./mol. This is thus an example of an exothermic " elementary reaction " possessing a considerable activation energy. Incidentally, the magnitude of this activation energy explains the failure of the reverse of $(d)$ to play an appreciable rôle in the kinetics of the decomposition—the *sec*-butyl radicals are consumed by the presumably much faster reaction $(c)$.

In conclusion, it may be repeated that the discovery of a Walden inversion caused by iodine atoms acting on *sec*-butyl iodide molecules is evidence in favour of the original hypothesis that substitution by free atoms in organic molecules is attended by optical inversion.

## Summary.

The homogeneous gas phase decomposition of *sec*-butyl iodide has been studied in the temperature range 238-276° C. The reaction was found to be of complex order, the two concurrent rate controlling steps being interpreted respectively as a uni-molecular dissociation into a free radical and iodine atom, and a bimolecular reaction of a *sec*-butyl iodide molecule with an iodine atom, yielding an iodine molecule and free *sec*-butyl radical. The rate constants for the two processes are given respectively by

$$8 \cdot 9 \times 10''e - \frac{39,420}{RT} \text{ sec.}^{-1}, \text{ and } 4 \cdot 25 \times 10''T^{\frac{1}{2}}e - \frac{16,820}{RT} \text{ (mol./cc.)}^{-1}\text{sec.}^{-1}.$$

The racemisation (of the undecomposed fraction) attending the decomposition of optically active *sec*-butyl iodide under the above conditions was also studied. The rate controlling process was found to be a Walden inversion caused by the substitution taking place on collisions between iodine atoms and *sec*-butyl iodide molecules. The rate constant for this process

was found to be $5 \cdot 00 \times 10''T^{\frac{1}{2}}e - \frac{13,780}{RT}$ (mol./cc.)$^{-1}$ sec.$^{-1}$.

A racemisation of active *sec*-butyl iodide by iodine at a soft glass surface was found at lower temperatures. The effect appeared to be caused by iodine atoms on the surface.

The results on the racemisation constitute evidence for the hypothesis that substitution by free atoms in organic molecules causes optical inversion.

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# THE ACCURACY OF THE LOG SECTOR METHOD OF QUANTITATIVE SPECTROSCOPIC ANALYSIS.

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The experience of the log sector method gained by the present authors was acquired in the course of investigations on

(i) The analysis of precipitates in powder form, an account of which is being published separately, and

(ii) Quantitative studies on corrosion involving the estimation of metallic elements present in solutions. (This work will, it is hoped, be described on completion.) These investigations were undertaken partly in order to study the possible accuracy of such methods, and, if possible, to improve the optical technique. It has been found possible in certain details to adopt methods which appear to us to be improvements on those described elsewhere, and of which a short description may therefore

be of service. Whilst avoiding undue reference to other papers, a recapitulation of the essential points of the method will bring out some aspects which are not always clearly stated.

The method is especially adapted to the estimation of metallic elements present as minor constituents of substances. For example, let an alloy consist mainly of element A with a small proportion of element B. The " internal standard " method of Gerlach and Schweitzer,[1] as developed by these and later workers, usually compares the intensity $I_B$ of a spectrum line of the minor constituent with that of a line of the major constituent, $I_A$. We show below that a relation representing the experimental results of Twyman and Hitchen [2] fairly closely is

$$\frac{I_B}{I_A} = kc^n,$$

where $c$ is the concentration of $B$, and $k$ and $n$ are constants for a reasonable range of concentrations up to a certain percentage which depends on the substances. The spectra have to be excited as closely as possible under the same conditions. The exact relation between $I_B/I_A$ and $c$ is found by trial experiments on alloys of known composition.

To determine the concentration of B in an alloy containing the same material, but in unknown proportions, it is then necessary merely to determine the relative intensities of the same two lines as found in the spectrum of the unknown when excited under closely similar conditions, and interpolate the result. This, of course, is the simplest possible case, but the method can be applied to much more complex conditions.

Apart from the control of the excitation of the spectra, the problem is therefore essentially of a spectrophotometric character, and is attacked most readily by the " log sector " method,[3, 4] a development of the photometric wedge. In this note we shall only deal with some of the difficulties incidental to photographic photometry.

The periphery of the Hilger sector is cut to conform to the numerical equation :

$$\log_{10} \theta = -0.3 - 0.2l,$$

where $\theta$ represents the angular aperture expressed as a fraction of $2\pi$, corresponding to an inward radial distance $l$ measured in millimetres from the circular part of the locus of the boundary. The sector is mounted in close proximity to the slit. A condensing lens, also close to the slit, projects an image of the source (arc, spark, etc.) into the prism system of the spectrograph, and uniformity of illumination of each spectrum line requires the absence of any vignetting of this image by the prism or associated lenses. When the sector rotates, the exposure at any point of the slit is intermittent ; moreover, the ratio of exposure period to darkness period in one cycle varies along the slit.

The work of Twyman and Simeon,[4] and Twyman and Harvey,[5] however, justifies the use of the Schwarzschild relation,

$$D = f(IT^p),$$

[1] Gerlach and Schweitzer, *Foundations and Methods of Chemical Analysis by the Emission Spectrum.* (Adam Hilger, Ltd.)

[2] Twyman and Hitchen, *Proc. Roy. Soc.*, **133A**, 72, 1931.

[3] Scheibe and Neuhausser, *Z. angew. Chemie*, **41**, 1218, 1928.

[4] Twyman and Simeon, *Trans. Opt. Soc.*, **31**, 169, 1929-30.

[5] Twyman and Harvey, *Trans. Opt. Soc.*, **33**, 1, 1931-32.

for the density $D$ found at any point in a spectrum line, where $I$ is the intensity, $T$ the total actual time of exposure, and $p$ a constant. In our case :

$$D = f\{I(\theta t)^p\},$$

where $\theta$ is the fractional sector aperture at the corresponding part of the slit, and $t$ is the time for which the source is burning. Now

$$\mathrm{Log}_{10}\{I(\theta t)^p\} = \mathrm{Log}_{10} I + p \log_{10} \theta + p \log_{10} t,$$

and in the case of equal densities found at some points in two close spectrum lines, " 1 " and " 2," on the same plate, for which the values of $p$ are identical, we should obtain :—

$$\mathrm{Log}_{10} I_1 + p(- 0{\cdot}3 - 0{\cdot}2l_1) = \log_{10} I_2 + p(- 0{\cdot}3 - 0{\cdot}2l_2),$$

which gives

$$0{\cdot}2p(l_2 - l_1) = \log_{10} \frac{I_2}{I_1}. \qquad . \qquad . \qquad . \qquad (1)$$

The lengths $l_2$ and $l_1$ are distances measured on the slit; they can be estimated from lengths measured on the plate by dividing by the linear magnification of the spectrograph.

*If this relation holds accurately it follows implicitly that the gradation of density towards the ends of long and short lines should be exactly similar.*

Further, if the relation holds for the threshold of perceptible density, then the difference in the lengths of two close spectrum lines should be proportional to the log of their intensity ratio. If, now, lines 1 and 2 correspond to elements A and B, and we assume that $I_B/I_A = kc^n$, then

$$0{\cdot}2p(l_2 - l_1) = \log_{10} \frac{I_2}{I_1} = \log_{10} \frac{I_B}{I_A} = \log_{10} kc^n. \qquad . \qquad (2)$$

If the above assumption is justified, we see that in a series of alloys such as discussed above, the difference in the lengths of a pair of lines, one due to the main constituent, and one to the minor, should bear a linear relation to the log of the concentration ; *i.e.*,

$$l_2 - l_1 = (0{\cdot}2p)^{-1}(\log_{10} k + 0{\cdot}434n \log_e c).$$

Differentiating, we obtain the numerical equation :

$$\delta(l_2 - l_1) = \frac{0{\cdot}434n}{0{\cdot}2p} \frac{\delta c}{c}, \qquad . \qquad . \qquad . \qquad (3)$$

which shows that a given error in estimating line-length should cause an error in estimating $c$ which is directly proportional to $c$. The error would *not* grow relatively more important as the concentration diminishes. Equation 2 gives a reasonable representation of the experimental results, which usually exhibit a nearly linear relation between $(l_2 - l_1)$ and $\log c$, so that this justifies the equation quoted at the beginning of this paper. One of us is making a closer study of the deviations from linearity sometimes found. So much for the general outline. We now come to our own experiences.

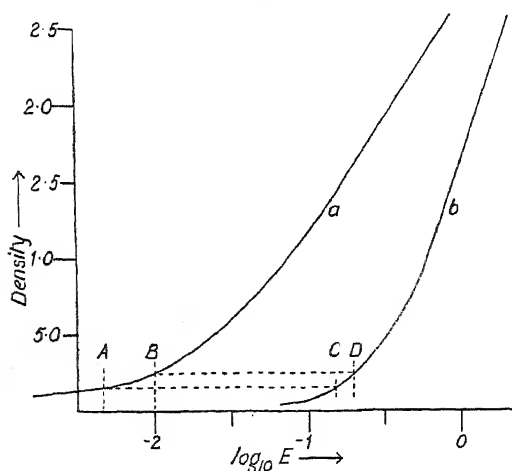### General Accuracy and Limiting Factors.

Twyman and Fitch,[6] in estimating copper present in proportions up to 1 per cent. as a constituent in steels, and using the arc as source, claimed an accuracy of one part in twenty of the copper content.

[6] Twyman and Fitch, *J. Iron and Steel Inst.*, **2**, 289, 1930.

Twyman and Hitchen's experience [2] in sparking solutions shows that an accuracy of about 10 per cent. can be obtained in estimating minor constituents of substances in solution. Occasionally, however, individual results were found to be in error by one part in five or worse. Our own experience in sparking solutions confirms this, but the experiments with the analysis of precipitates, using the arc, showed considerably larger possible errors in individual results, of the order of 30 per cent. of the minor constituent. Now we find that an accuracy of 5 per cent. in estimated concentration (one part in twenty of the minor constituent) requires an accuracy of about 0·1 mm. in the difference of line lengths. Our initial trials in measurement of lines revealed personal errors of considerably greater amounts, of the order of 0·3 mm. It was therefore clear that while in some cases the irregularity of the source (as in arcing powders) is the factor limiting possible accuracy, the line measurement was likely to be a relatively important source of difficulty in other cases.

## The Threshold of Blackening.

At the "end" of the line we find scattered silver grains with a somewhat irregular distribution ; these gradually become indistinguishable from the general field of the plate, in which there is usually a slight amount of fog. It is clearly of the utmost importance to reduce such fog to a minimum. This can best be effected by careful development, as will be described later, but with fast plates a trace of fog appears to be inevitable.

It has been found that the ends of lines on fast plates are liable to be indeterminate. This can be explained with reference to Fig. 3, which shows some typical characteristic curves of photographic plates. The abcissæ of such curves are units of log (exposure), and since the exposure varies logarithmically



Background
fog density.

(a) Very fast plate   .   .   0·09
(b) Process   ,,   .   .   0·04

Fig. 1.—Typical characteristic curves.

along the slit, we may substitute an evenly divided scale of line-lengths in place of the log E scale. The form of the foot of the characteristic curves can thus be made to predict the manner in which the density falls off at the end of a line.

Fig. 1, curves (a) and (b) relate to a fast plate and a process plate respectively, and it will be seen that the length of line AB, near the end, in which the fast plate acquires a given change of density is great as compared with the corresponding length CD for the process plate. The effect with a fast plate is to give an attenuated end or "tail" to the line, and this may be mistaken for a double end-point in fogged or over-developed plates.

Of the plates we tried, we found that Ilford Process and Panchromatic Process plates gave the most definite end-points ; judging from the figure, this would appear to be associated with a steep slope at the foot of the characteristic, and a low background fog density. In some cases, however,

we have been compelled to use fast plates, such as the Ilford Monarch, in order to reduce the exposure required in sparking solutions. A compromise has therefore been necessary in such cases, and we have been compelled to study very carefully the factors affecting judgment of the end-points.

The relation found between measured values of $(l_2 - l_1)$ and log $c$ deviates from linearity at low concentrations when using Ilford Monarch plates. Short lines are longer than would be anticipated from equation (2), as a result, probably, of the additive effect of "background." This does not agree with Twyman and Harvey's observation that when *slow* plates were used the short lines were longer than would be anticipated from the Schwarzschild relation, but that it was not so with fast plates.

With slow plates the slope of the straight line portion of the H and D curve is said to be dependent on the intensity employed.

With fast plates we have observed that the end-points of long lines are noticeably sharper than those of short lines, which seem to terminate more gradually. This may be due to slight deviations from the Schwarzschild relation. On the other hand, the exposure at any point of a line in a spectrum band is determined not only by the intensity of the line itself and the sector aperture, but also by the presence or absence of any continuous spectrum, or stray light derived from internal reflections in the optical system, halation in the plate, and so on. Marked effects due to stray light are well known to occur in spectrum photographs in the neighbourhood of intense lines. The effect of such additional light near a line to be measured will obviously lift a greater portion of its length over the threshold of density, and the lengthening is likely to be more marked with weak lines than with intense ones, since the effective aperture of the background light is clearly being reduced far more by the sector at the end of a long line than at the end of a short one. The effect might occur even in the absence of background effects appreciable in a photograph. The initial calibration will take account of such effects only if the conditions of the test experiments and calibration curves are sensibly identical.

Effects due to inaccuracy of the Schwarzschild relation, or to deviation from the relation between "line intensity" and "concentration" assumed above, may produce a departure from linearity at the lower end of the curve connecting $(l_2 - l_1)$ and log $c$, but this again need not cause error if the calibration is carefully performed.

*Development.*—The technique of development was substantially the same as that of previous workers (*vide* Twyman and Simeon, p. 176). The developer was Caustic Hydroquinone with more than the usual amount of Potassium Bromide, and a short development, $2\frac{1}{2}$ minutes, was allowed in order to keep down the background fog. Four minutes development produces fog of appreciable amount for present purposes.

### Observation of End-points.

Microphotometric determinations of density and special devices involving the making of positives, such as Merton's,[7] were rejected for purposes of initial studies on account of the additional time and complication involved. Direct measurement of lines was therefore tried.

The first method was to use a Ramsden eyepiece (Fig. 2) giving a magnification of × 10. This was fitted with a telecentric stop, and a 2 cm. scale divided to 0·1 mm. To prevent damage to the scale it was fitted glass side outermost; hence the necessity of the stop, in order to avoid parallax.



FIG. 2.—Eyepiece with telecentric stop.

The photographic plate was placed on a sheet of opal glass illuminated from behind, and a $\frac{1}{2}$ cm. mark (which was

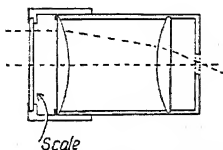[7] Merton, *Proc. Roy. Soc.*, 106A, 378, 1924.

slightly longer than the other divisions) was placed against the end of the line (Fig. 3). The position on the scale at which the fully exposed part of the spectrum occurred then gave a measure of the line length. When the scale was placed along the spectrum line, it was hopeless to attempt to determine the end-point.

We had formed the opinion that some singularity near the end of the line might sometimes be selected as an end-point, and that in, say, five consecutive observations the same point might be chosen each time, whereas if observations were made consecutively on a number of different lines in turn, and then repeated, so that each individual line was measured five times in all, the observations would prove to show less consistency. This point was carefully tested by a set of readings on zinc and copper spectrum lines in some seventeen spectra. Consecutive readings on each line in turn gave a mean error of 0·14 mm. ; when the readings on the same set of lines were made non-consecutively, the error rose to 0·18 mm.
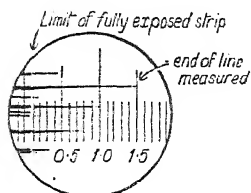


Fig. 3.—Appearance of spectrum lines and scale.

Singularities of the above type were found often to be due to minute specks of dirt or scratches in the film. Washing only with changes of *distilled* water gave an improvement, but dirt accumulated on drying in spite of all precautions. Accordingly, the plates are now measured wet, immersed in a small tank, with the help of a reversed measuring microscope (Fig. 4). The objective projects an image of the crosswires into the plane of the plate ; both spectrum lines and crosswire image are then examined with the aid of a low-power magnifier.

The field of the plate is also illuminated by light reflected from a glass plate, P, in the figure. Under these conditions the *contrast* between the crosswire image and background can be controlled so that it is more comparable with the appearance near the end of the line. It is our experience that the system is much easier to use on this latter account. In addition, parallax is completely removed, and minor irregularities in the film become invisible. The walls of the tank should be constructed of reasonably good selected plate glass. The consistency of settings with this arrangement has been found to be considerably better than can be obtained with the scale.

The same method has been used with success for the measurement of the diameter of the faint rings



Fig. 4.—Apparatus for measuring lines.

which often occur in electron diffraction and X-ray photographs, for which the magnifying powers of practically all compound microscopes fitted to measuring microscopes are too high.

**Sharpening of End-points by Reduction or Intensification.**—We have made a number of trials of this proposal in the hope that the relatively diffuse end-points obtained with fast plates might be sharpened, but it was found that quite large lengths of line are apt to disappear before any appreciable increase of contrast is effected.

Intensification, with or without previous reduction, was also tried with no success in improving contrast. We have not, however, tried reduction with slow plates ; the end-points seemed already sufficiently definite when these were used.
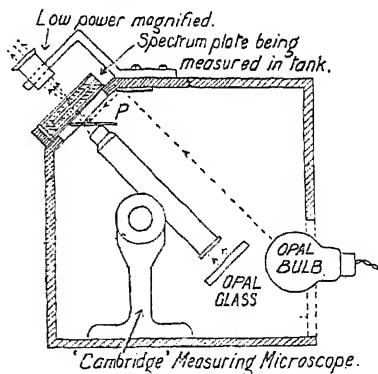
**Background Caused by Continuous Spectrum.**—More especially in work with the arc, the spectrum lines to be studied are often imposed on more or less continuous spectrum due to the white-hot poles, or parts of band spectra occurring in the same region.   There will be, for any one line, some optimum slit width for which the ratio of line intensity to background intensity will be a maximum, and this effect was carefully studied in our work with the arc.   It is clear that the intensity of a line will at first increase fairly rapidly with slit width until the geometric image is of width comparable to the diffraction image, and will thereafter tend to become constant, while the intensity of the continuous background will show a slow increase, and is always proportional to the slit width.

The effect of the sector would, of course, be expected to reduce the "continuous" below the threshold of photographic action before the "line," but it was our experience that the residual background effect was more serious when the spectrum itself showed more or less "continuous" radiation, and efforts were made to reduce it.   The special packing of graphite electrodes with the salt, and the admixture of the salt with Ammonium Sulphate were found to be useful in reducing the intensity of the Cyanogen bands in the carbon arc.

Trials were also made of a device by which the image of the arc was brought on a diaphragm with a small aperture admitting only the light from the flame of the arc, and thus obstructing light from the white-hot poles.   The image of this aperture was then projected into the prism system of the spectrograph.   The device was to some extent useful, but it was considered to introduce too much uncertainty owing to the wandering of the arc, and the uneven development of different spectrum lines in various parts of the flame.

Difficulties of the above character were less troublesome in using electrodes of pure silver or copper.

**Tests on the Sector.**—The whole accuracy of the experiments is naturally dependent on the precision of the figure of the sector edge.   In using a sector in early experiments it was found that the gradation of density of lines was a little uneven, the effect being that a number of very faint bands traversing the spectrum in the direction of the dispersion, somewhat similar to the effect which might be given by irregularities of the jaws of the slit.   After many efforts to trace other sources of the error, the figure of the sector itself was tested.

Suppose that the law of the sector, given, as above, by the relation

$$\log_{10} \theta = - 0.3 - 0.2l,$$

is subject to slight variation locally, so that, for example, a given value of $\theta$ corresponds to a value of $l$ which is greater than it should be.   This might correspond to the removal of a part of the edge.

Let this value of $\theta$ correspond to the threshold exposure for a particular spectrum line under the conditions of experiment.   The exposure depends solely upon $\theta$, and the end of the line will therefore be found at the corresponding value of $l$.   Hence the errors in the radii of the sector will give equal errors in the lengths of lines (assuming unit magnification is given by the spectrograph).

The sector was mounted in a dividing head and observed by a Cambridge measuring microscope, both clamped to a rigid iron table.   About half the circumference of the sector (as can be seen from the sector formula) has a circular locus, and the centering was adjusted until the image of this part of the sector showed no movement relatively to the crosswires on rotation of the head.   After checking the centering as described, the angular position of the sector and the inclination of the axis of the microscope were mutually adjusted until the locus of the focus of the microscope lay exactly along the radial portion of the sector.

The errors found in $l$ were on the whole small, reaching positive and negative maximum values of $+ 0.15$ and $- 0.10$ mm. respectively, but

they accounted entirely for the bands observed in the spectrum, the centres of the light bands corresponding to minima and the centres of dark bands to maxima of the curve of errors.

The makers of the sector, Messrs. Adam Hilger, Ltd., took up this matter with their usual courtesy and thoroughness, and supplied a new sector which showed no bands in the spectrum, and correspondingly small errors when tested on the dividing head. The errors did not vary by more than + 0·08 mm. and − 0·02 mm., nor did they fluctuate widely so as to cause visible bands. In one place, however, an error of + 0·17 mm. existed, and was subsequently corrected. Residual errors can be precisely compensated for from the calibration curve when necessary, since, as pointed out above, the error in line length is equal to the error in radius.

## Conclusions.

It appears to us that given a satisfactory means of exciting the necessary spectra (for example, the sparking of solutions), there is nothing in the photometric part of these quantitative methods which need cause errors much above 5 per cent. of a minor constituent. A great deal naturally depends on the circumstances of special cases, the availability of suitable spectrum lines for study, etc., but there is no doubt that spectroscopic methods can be used to great advantage in many cases where chemical methods are inadmissible.

The Authors are indebted to Messrs. Adam Hilger, Ltd., for the loan of part of the apparatus used in this research, and to Mr. F. Twyman, F.R.S., for his interest and advice.

## Summary.

The paper summarises the experiences of the authors in employing the " log sector " method of spectroscopic quantitative analysis, and discusses the difficulties incidental to the photographic photometry involved. A special technique of line-length measurement is described, and also the apparatus employed. The error in estimating a minor constituent need not exceed 5 per cent. of its amount as far as photometric factors are concerned.

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# AN INVESTIGATION INTO THE USE OF THE LOGARITHMIC SECTOR FOR THE QUANTITATIVE ANALYSIS OF PRECIPITATES.*

By E. G. Knowles, D.I.C., M.Sc. (*Research Scholar*), and L. C. Martin, D.I.C., A.R.C.S., D.Sc. (*Assistant Professor of Technical Optics in the Imperial College of Science and Technology*).

Many methods of using the spectroscope for quantitative analysis have been tried during the last few years. In the case of alloys [1] and solutions [2] the log-sector method [3, 4] has been used with success to

[1] Twyman and Fitch, *J. Iron and Steel Inst.*, **2**, 289, 1930.
[2] Twyman and Hitchen, *Proc. Roy. Soc.*, **133A**, 72, 1931.
[3] Scheibe and Neuhausser, *Z. ang. Chem.*, **41**, 1218, 1928.
[4] Twyman and Simeon, *Trans. Opt. Soc.*, **21**, 169, 1929-30.

ncrease the relative accuracy of the photometric part of the measure-
ment, but apart from the Ratio-quantitative method of Judd-Lewis [5]
comparatively little has been done upon the analysis of powders.

In the work described in this paper, the problem concerned chemical
co-precipitation. For example, when barium is precipitated with an
alkali sulphate, some of the alkali metal is always carried down with the
precipitate of barium sulphate ; it appeared possible to use the spectro-
scopic method to study the amount of alkali metal co-precipitated.
Further problems concern the co-precipitation of zinc with copper
when the latter is precipitated as the sulphide, and the precipitation of
magnesium with calcium as the oxalate. Studies of this kind are of
some importance in quantitative chemical analysis, and it was hoped
that the work might further result in improvements in the accuracy of
the method as applied to such problems.

The estimation of potassium co-precipitated with barium has already
been studied [6] by chemical methods, and the spectroscopic method has
been applied [7] to the estimation of magnesium precipitated with calcium.

In the present paper the internal standard method,[8, 4] which naturally
suggests itself, is shown to present undue difficulties as applied to
" potassium with barium," so that the main results concern " zinc with
copper." A commencement was made on the " magnesium with
calcium " problem, but the work had to be terminated before this was
completed.

## Estimation of Potassium in Barium Sulphate.

The proposed method of determining the quantity of potassium in a given
sample of barium sulphate precipitate was to prepare in the first instance a
series of " standard " mixtures of barium and potassium sulphates contain-
ing varying small proportions of potassium. The spectra of these mixtures
would then be photographed, under standard conditions, with a Hilger " log-
sector " rotating closely in front of the slit of the spectrograph, and the
difference of length of the selected lines, a potassium line, and an " internal
standard " line due to barium, would be correlated with the proportion of
potassium. An additional photograph of the spectrum of the given barium
sulphate precipitate would give a certain difference between the lengths of
the selected lines, which would point to a certain proportion of potassium.
The spectroscopic methods adopted in the first instance closely follow those
described by Twyman and his collaborators.[1, 2, 4]

A closely analogous procedure naturally suggests itself in the other two
cases, but it is of course important that the chemical state of the materials
in both the standard mixtures and the precipitates should be the same.
To ensure this, the precipitates and the synthesised mixtures were always
sulphated.

Since the determination of potassium in this way was not successful,
the particulars of the preparation of the standards, etc., from " Specpure "
Barium Chloride and Potassium Chloride will not be described, but in
spite of the failure a number of lessons were learnt from the attempt. It
may be mentioned that the series of standard mixtures contained the follow-
ing percentages of potassium by weight : 0·92, 0·46, 0·047, 0·0047, 0·00047.

[5] Judd Lewis, *J. Soc. Chem. Ind.*, 25th March, 1932.
[6] Nicholson, *Trans. Amer. Chem. Soc.*, 1910.
[7] Popoff, Waldbauer and McCann, *Ind. Eng. Chem. Anal. Edn.*, 4, 43, 1932.
[8] Gerlach and Schweitzer, *Foundations and Methods of Chemical Analysis by the Emission Spectrum.* (Adam Hilger, Ltd.)

**The Production of the Spectrum.**

A medium Hilger quartz spectrograph (E 316) was used, and the image of the source was projected into the prism system with a quartz lens. Vaporisation with the aid of the *arc* was first tried using graphite, then copper, electrodes. The main difficulty at once encountered with the graphite was the masking of the lines by the cyanogen bands, and the continuous spectrum.

Following a suggestion of Dr. Judd Lewis, the sample was mixed with Specpure Ammonium Sulphate and packed into the lower (positive) pole of a pair of copper electrodes, which had been drilled to a depth of about 2 mm. With a current of 5 amps. the potassium lines at $\lambda 4047$Å and $\lambda 4044$Å appeared, but were subject to some interference by near copper lines. With lower current strengths the lines did not come out well.

Various other conditions were tried, such as packing the upper pole with the mixture, but it was not found possible readily to obtain a satisfactory photograph of a potassium line free from interference by background or masking effects.

The *oxy-hydrogen flame* was tried later. In the hands of Mr. H. Ramage, flame spectra have been used for quantitative methods [9] in the estimation of metallic constituents in biological tissues, and for other purposes. We are indebted to him for giving us the benefit of his experience.

Our own first trials were made with a burner of the welding type giving a rather long thin flame. Forty milligrammes of the salt were spread over a filter paper of the " ashless " type which was folded and fed into the flame at the rate of combustion. Such papers are free from potassium, but contain a little calcium and sodium. The burning appeared to be steadier if the papers were first moistened with distilled water. Unfortunately barium gives only one line in the flame, at $\lambda 5535$Å, and this occurs in the midst of a complex band spectrum.

It was found that the salt fused into beads which dropped off irregularly, thus giving very different effective exposures, more particularly for the barium line. The potassium lines were very faint. Although the image of the flame was projected into the prism of the spectrograph, it was too large not to be partly screened. This in itself would cast some doubt upon the accuracy of a photometric determination.

Mr. Ramage was good enough to examine the flame spectra of a series of the standard mixtures, using his own apparatus and technique. His oxy-coal gas flame was much shorter, and the image of the flame was focussed on the slit. In no case could 10 milligrammes of the barium be completely volatilised in one paper, although the compound was subject to considerable heating sufficient to volatilise all the potassium. The result was that the spectra of the mixtures containing increasing proportions of potassium gave a satisfactory regular increase in the intensity of the potassium lines, but the intensity of the barium line and bands varied irregularly.

Mr. Ramage suggested the following expedients for trial : to divide the 10 milligrammes between two filter papers ; or to mix the salt with say 40 milligrammes of an organic substance, such as starch, free from minerals ; but this part of the work had to be terminated before these suggestions could be carried out, although a trial was made of mixing the barium salt with an equal quantity of ammonium sulphate before burning it.

Owing to the uncertainties due to the difficulty of volatilising the barium and the masking of the only line, it appeared that the method of the internal standard could not be effectively applied by the use of the flame, and it was resolved therefore to turn to the case of zinc and copper.

Of course the possibilities of work with the potassium and barium compounds are by no means exhausted. Another substance might be introduced as an auxiliary standard in using the flame method, and the

[9] H. M. Fox and H. Ramage, *Proc. Roy. Soc.*, 108B, 157, 1931.

use of silver poles for the arc could have been tried. It was felt, however, that an easier problem should be dealt with first of all. It is evident that each problem must be studied on its own merits.

## Estimation of Zinc co-precipitated with Copper.

In this experiment greater success was obtained, and some chemica details will be given.

When copper is precipitated as the sulphide and zinc is present, some zinc is carried down with the copper, as in the analysis of brasses ; the amount of zinc appears to depend on the relative acidity of the solution. It was decided to investigate this point.

The most general ratio of copper/zinc encountered in analysis is 60/40. Two solutions were made up from copper sulphate and zinc sulphate (B.D.H., A.R. chemicals) such that by taking 10 c.c. of each a suitable amount of the metals in the correct proportion was obtained.

### Preparation of Precipitates.

In carrying out the precipitation, the necessary hydrochloric acid was added to the 10 c.c. portions, and the whole made up to 250 c.c. This was heated to boiling-point and sulphuretted hydrogen bubbled through for half an hour. The precipitate was washed three times with $H_2S$ water, and then washed after transferring to the filter until free from chloride, as shown by the washings giving no precipitate with $AgNO_3$ solution after the hydrogen sulphide had been removed by boiling. When free from chloride the precipitate was removed to an evaporating dish and evaporated to dryness with concentrated nitric acid and a little bromine. The residue was moistened with a little sulphuric acid and the excess acid fumed off, care being taken to avoid over-heating, since zinc is rather volatile. The residue was dissolved in distilled water, filtered, and evaporated to dryness. Removing the residue from the dish, it was ground to ensure homogeneity and placed into a bottle.

Precipitations were done in eight acid concentrations from 1 per cent. to 8 per cent. HCl, two precipitations (A and B) being made for each strength of acid, as a check.

### Preparation of Standards.

" Specpure " solutions of Copper chloride and Zinc chloride, obtained from Messrs. Adam Hilger, Ltd., were used. The necessary amounts of the two solutions were measured out and evaporated to dryness in platinum dishes. The residue was moistened with sulphuric acid and the excess acid fumed off. This was repeated, care being taken as before not to use more heat than necessary. When cool, the salt was dissolved in distilled water and evaporated to dryness. The residue was then ground in an agate mortar. To prevent contamination all operations were conducted under clock-glasses.

### Excitation of the Spectrum.

An arc between graphite electrodes was first tried, and it was found possible to obtain sets of measurements, but on examination of the results for the standard mixtures it was found that no satisfactory degree of regularity had been obtained. Following a suggestion by Dr. Judd Lewis, silver electrodes were then tried. The lower one was tapered slightly, and a small flat formed on it, on which was placed a pellet of the salt. Pellets of uniform size (about 10 mgm.) were prepared by means of a small steel die ; they were only slightly smaller than the flat. The gap of the arc and the positions of the electrodes were carefully controlled by optical means. The arc was struck by drawing a third silver rod across the poles. The expedient of mixing the salt with an equal weight of ammonium sulphate before grinding and forming into pellets was also tried. This increased the background intensity, but gave steadier conditions.

### Lines for Use.

The best zinc lines for use are $\lambda4722$Å and $\lambda4810$Å, since silver gives a very marked continuous background in the region of $\lambda3300$Å near the zinc lines $\lambda3302$Å and $\lambda3344$Å.    The best copper lines appear to be $\lambda\lambda5153$, 5105, 4758 and 4704Å.    All these are selected with the aid of Kaysers' " Tabelle der Hauptlinien der Linienspektra Aller Elemente " as occurring more strongly in the arc than in the spark.    The lines of the ionised atoms which occur more strongly in the regions near the poles of the arc, where there are comparatively large potential gradients, would appear to have intensities, relatively to the " arc " lines or lines of the neutral atoms, which are likely to be dependent upon small variations of the conditions.

### Plates.

The plates employed were Ilford Process Plates.    Some trials were made with Ilford Rapid Process Panchromatic Plates.

### Exposures using Standards.

The conditions of arcing the pellets of the standard mixtures were :—

Current        = 2·5 amps. on 110V. mains ; upper pole + ve. (starting
                       current = 4·5 amps immediately reduced).

Arc gap       = 1·5 mm.
Slit width     = 0·03 mm.
Exposure     = 3 mins.
Sector speed = 250 r.p.m.

The difference in lengths of lines of zinc and copper for several line pairs are plotted against the logarithm of the percentage of zinc in Figs. 1 and 2. The following are the percentages of zinc to copper used in the "standards": 2, 1·75, 1·5, 1·25, 1·0, 0·75, 0·5, 0·25, 0·1, 0·075, and 0·05 per cent.
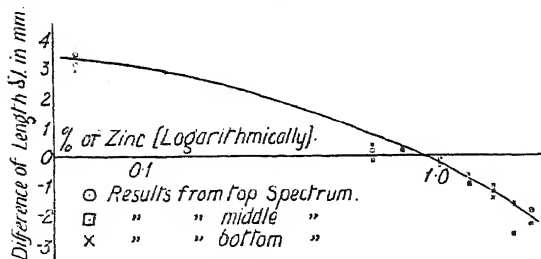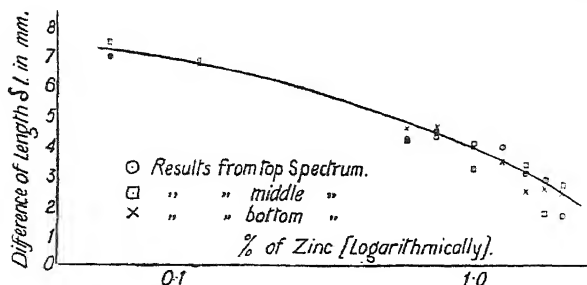


FIG. 1.—Line pair $\begin{cases} \text{Cu } \lambda4704\text{Å.} \\ \text{Zn } \lambda4722\text{Å.} \end{cases}$

○ Results from Top Spectrum.
□ ,,      ,,   middle ,,
× ,,      ,,   bottom ,,

### Exposures with Precipitates.

The conditions of arcing with the precipitates formed in the eight different concentrations of HCl were identical with the above.    Using the line pair Cu $\lambda4704$Å, Zn $\lambda4722$Å, the differences of length $\delta l$, shown in the following table, were obtained for the two precipitates A and B for each concentration.



○ Results from Top Spectrum.
□ ,,      ,,   middle ,,
× ,,      ,,   bottom ,,

FIG. 2.—Line pair $\begin{cases} \text{Cu } \lambda5153. \\ \text{Zn } \lambda4810. \end{cases}$

Using these values of $\delta l$ and Curve 1 for the standards, the curve for the variation of the zinc content is shown in Fig. 3.    The rise in the zinc content at the higher concentrations appears to be confirmed in each case.

| Per Cent. of HCl. | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. |
|---|---|---|---|---|---|---|---|---|
| $\delta l$ ppt. A | — 1·65 | — 0·81 | — 0·42 | 2·65 | 1·97 | 0·42 | 1·84 | 1·65 mm. |
| $\delta l$ ppt. B | — 1·74 | — 0·03 | 2·0 | 2·79 | 2·65 | 1·72 | — | 2·00 mm. |

Consistency of Results.

Curves 1 and 2 embody the results of determination on three separate exposures for each of the standards. A general inspection of the figures would suggest that the accuracy of the mean curves is fairly good, but some individual points lie off the curve by horizontal distances which correspond to errors up to 40 per cent., or more, of the zinc content. The same is true of other curves, examples of which are shown in Figs. 4 and 5.



FIG. 4.—Line pair $\begin{cases} \text{Cu } \lambda 4704\text{Å.} \\ \text{Zn } \lambda 4722\text{Å.} \end{cases}$

FIG. 3.

FIG. 5.—Line pair $\begin{cases} \text{Cu } \lambda 5153\text{Å.} \\ \text{Zn } \lambda 4810\text{Å.} \end{cases}$
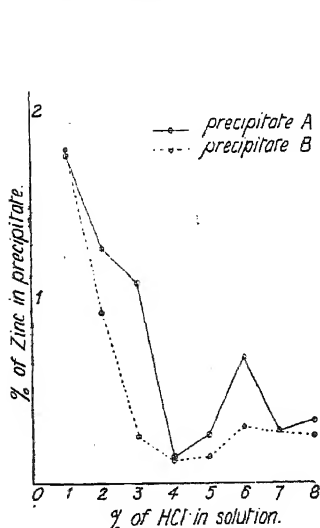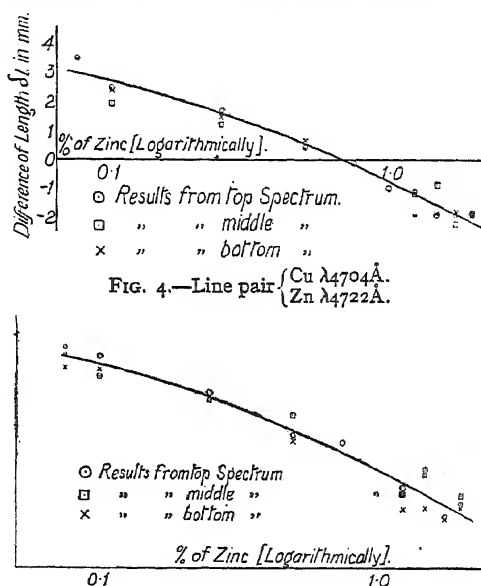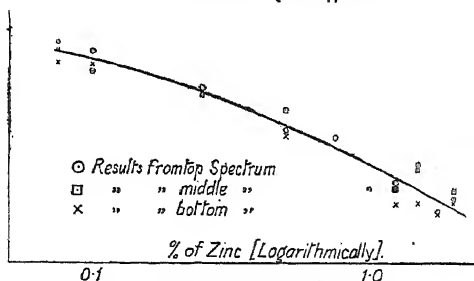
This does not give great confidence in individual results for the trial precipitates. Twyman and Hitchen, using the method of sparking solutions, recorded such accidental errors up to 20 per cent., so that the arcing of powders seems (as was expected) to be even more difficult to control.

It will be noticed that an accuracy of, say, 5 per cent. of the zinc content requires an accuracy of the length of a line between 0·1 mm. and 0·15 mm. It has been pointed out elsewhere that the error in the amount of the minor constituent, expressed as a fraction of such amount, due to the given error in the line length does not vary greatly with the concentration. It is, of course, well known that arcs are apt to burn unsteadily but it might be hoped that the relative intensities of the arc lines of the material would not vary greatly from one experiment to another.

The work described in the present paper was performed mainly in the session 1932-33. About the same time, Twyman and Hitchen,[10] used an

[10] *Spectrum Analysis with Hilger Instruments*, pp. 47-48, 1933. (Adam Hilger, Ltd.)

REVIEWS OF BOOKS

arc method in which two or three grams of a powdered ore are completely burnt from a hollowed-out graphite electrode, the arc being far enough from the sector and slit to ensure that over-exposure does not result from the comparatively long time required to consume the sample.

A similar method was tried in the present work when dealing with Potassium in Barium sulphate, *i.e.*, an effort was made completely to consume samples of the standards in the arc. It was found, however, that the ratio of the background density to the density of the potassium lines became too great, and the method was abandoned. It was not tried, for that reason, when dealing with zinc and copper; but the experience of Twyman and Hitchen suggests that it would have been of service in this case. We were content, in our own work, to control the constancy of the arcing conditions as carefully as possible and to give a standard exposure.

The technique of development, etc., was closely similar to that adopted by Twyman and his collaborators. During the course of the work, however, various expedients were tried which proved of some value, and these are being described in a second communication by the present writers in collaboration with S. A. Burke. Reference may be made to that paper for details of the photometric aspects of the problem.

We are greatly indebted to Messrs Adam Hilger, Ltd., for the loan of certain apparatus; also to Dr. S. Judd-Lewis, Mr. Hugh Ramage, Dr. H. F. Harwood, and Mr. F. Twyman, F.R.S., for their interest and valued advice.

## Summary.

Quantitative measurements of chemical co-precipitation are attacked by the methods of quantitative spectroscopic analysis, and results are given for the precipitation of zinc with copper when the latter is precipitated as the sulphide from solutions of varying acidity.

# REVIEWS OF BOOKS.

**Einführung in die Lehre von den Kolloiden.** Unter Mitwirkung zahlreicher Fachgenossen herausgegeben von Prof. H. BECHHOLD. (Dresden and Leipzig, 1934: Theodor Steinkopff. Price RM. 9. Pp. 160.)

In 1932 a short course on Colloids was held at the " Institut für Kolloidforschung " in Frankfurt a. M. before an audience drawn from a wide circle, and the present book gives the substance of the lectures then delivered. This genesis explains a feature unusual in an elementary work of about 150 pages of text: seven authors contribute nine chapters, entitled: I. What are colloids ? (H. Bechhold) ; II. The preparation of colloidal systems (R. Schwarz) ; III. Colloid particles as physical molecules (L. Hock) ; IV. Interfaces and processes at interfaces (E. Heymann) ; V. Sols, gels and coagels, especially their non-electrical and non-optical properties (L. Hock) ; VI. Electrical properties of colloids (E. Heymann) ; VII. Separation and purification of colloids (F. Erbe) ; VIII. Optics of colloids (E. A. Hauser) ; IX. X-ray investigation of colloids (R. Brill).

A feature of the book which will strike all readers and may be an attraction to many of them is the almost complete avoidance of mathematical formulæ. Whether anything is really gained by putting quantitative statements regarding, *e.g.*, the Brownian movement or the diffusion

coefficient of particles in words rather than symbols, may be doubted ; perhaps the authors and editor hope that the conscientious " general " reader would try to grasp what appears as text while he would *a priori* skip formulæ.

Unlike some larger collective works, the book achieves a remarkable unity and provides a survey of modern colloid chemistry which, on the whole, is surprisingly well-balanced. Rival theories are stated with great fairness, *e.g.*, those advanced to account for the electric charges on colloid particles, which are summarised in one of the best chapters of the book· That on the X-ray investigation of colloids is an equally remarkable piece of lucid exposition. Balance is not quite so well preserved in the chapters on optics and on separation and purification : the former, which begins with the simple microscope and winds up with the most recent vertical illuminators and fluorescence instruments attempts a good deal more than is possible in the space of thirteen pages, while the latter assigns an exaggerated importance to ultra-filtration.

These, however, are very slight blemishes, and even less serious is a certain arbitrariness in spelling well-known French names : Devaux appears as " Deveaux " and Duclaux as " Ducleaux ". The book provides an almost royal road to modern colloid science, and can be thoroughly recommended to the numerous readers who, without intending to specialise in it, find some knowledge of it increasingly necessary in their own work.

E. H.

**The Diffraction of X-Rays and Electrons by Amorphous Solids, Liquids, and Gases.** By J. T. RANDALL, M.Sc. London, Chapman and Hall, Ltd. Pp. xii + 290, with 197 illustrations. 1934.

There can be no doubt that an immense amount of careful work has gone to the making of this book, and that the result is well worth it. The first hundred pages, roughly, deal with concepts and methods now largely accepted as classical ; rather than tarry over them, it may be more illuminating to follow the author through the second part of his book, in which he gets to grips with phases more truly amorphous, as well as mesomorphic. Here he is on fairly new ground. For example, in his discussion of the liquid state, it becomes clear from the work of Bernal and Fowler upon the constitution of water that co-ordination exists within extremely minute (three-dimensional) regions : different kinds of water molecules are not postulated ; what is maintained is that they are differently packed in the various types of water. The application of electronic diffraction experiments to liquids is seen to be valuable (on account of the low power of penetration) for the investigation of surface phenomena.

The chapters which deal with the solid state bring together a mass of material rarely assembled between the same two covers. Glass, amorphous carbons, coal and phosphorus all come in for their share of attention. Incidentally, it looks as if the author was at least sceptical of the " peat-to-anthracite " theory of coal formation. If the evidence for this view is confirmed, an interesting situation will arise, since palæobotanists (so the reviewer understands) are loitering with intent to return—after a period of doubtfulness—to this very same idea of carbonaceous development. In this connection, vitrain and durain can scarcely be called " two distinct classes of coal." Certainly they are distinct, but Stopes and others have

been meticulously careful to stress their nature as constituents, in contrast to claiming class properties.

On page 186 it would seem that the author is on slightly dangerous ground. *Reststrahlen* do not register the characteristic frequency of a substance, but a frequency which is a complicated function of the true oscillations (as is capable of calculation by means of the Havelock-Försterling correction). Owing to the large number of factors involved, this function is very sensitive to small changes in certain terms : approximate co-incidence of *reststrahlen* is not a very safe criterion of even " first-order " structure. The main trouble is that, unless refined absorption positions can be accurately established, the very features of co-ordination which are relevant may escape detection.

The account of liquid crystals in Chapter IX. is most welcome. Naturally, it follows the lines of the Faraday Society's recent report, but it is none the less desirable for that. Also an opportunity is provided for displaying to great advantage the fascinating micro-photographs of mesomorphs obtained by Dr. A. S. C. Lawrence.

Apart altogether from details, the value of a book like Mr. Randall's lies largely in the recognition of the paramount part played by the conservation of molecular complexes through change of state. This is a matter of fundamental importance to everybody : a very wide circle of readers therefore should appreciate these pages.

F. I. G. R.

**A Comprehensive Treatise on Inorganic and Theoretical Chemistry·** By J. W. MELLOR, D.Sc., F.R.S. Vol. XIII. Fe (Part II.). (London : Longmans, Green & Co., 1934. Pp. viii + 948. £3 3s. net.)

Some four hundred pages of volume twelve of this work were devoted to the metallurgy of iron and to certain properties of iron and the iron-carbon alloys. The nine hundred pages of the present volume do not suffice to carry us to the end of the story of iron. They continue the description of the iron-carbon alloys, discuss the corrosion and passivity of iron and describe the alloys and intermetallic compounds. Amongst the numerous ordinary iron compounds room is found only for the oxides and their hydrates and the ferrites and ferrates.

The hundred-page interesting and valuable section on the corrosion of iron and steel is introduced by Pliny's remark that nature has inflicted the punishment of rust upon iron, a punishment stated to cost 500 millions per annum. Members of the Faraday Society will recall with pleasure the pioneer work of a past President of the Society on the production of alloy steels, including the punishment-free chromium steels. The vast detail and intensity of modern research is exemplified by the fact that a seemingly simple, though very important, substance like ferric oxide needs sixty pages. But perhaps one should not be surprised, for to-day a whole book can be written about a reaction like the combination of hydrogen and oxygen. In connection with ferric oxide, one is pleased to observe the author's own work peeping out through the use of the word " I."

This volume shows that, for the present author at any rate, there is nothing unlucky about the number thirteen.                C. H. S.

# MEASUREMENT OF THE ELECTRICAL RESISTANCE OF YARNS AND CLOTHS. VARIATION IN THE RESISTANCE OF SILK WITH $p_H$.

By W. S. Denham, E. A. Hutton, and T. Lonsdale

## Introduction and Summary.

This paper describes a new method of measuring the insulation resistance of yarns and fabrics and gives the precautions, chiefly those of humidity control, that have to be observed in order to obtain reliable results with materials of this character. These methods of measurement are then used to reveal variations in the electrical resistance of silk with electrolyte content, which are related to its behaviour as an amphoteric protein.

## Method of Measurement.

An extensive study of this subject has been made by Murphy and co-workers,[1-4] working principally on cotton. They prepare the yarn for test by winding it round two parallel metal rods which act as electrodes. The resistance measured is thus the longitudinal resistance of the threads stretched between the two rods.

In the method now described, which was developed for routine work in 1924, the yarn or cloth under test is sandwiched under pressure in a layer between two stainless steel electrodes. The resistance measured is thus the transverse resistance of the material upon which its effectiveness as an insulator mainly depends. This method has the further advantage over that described by Murphy in that it is better adapted to reveal in the yarn or fabric the presence of occasional small spots or impurities of low resistance.

## Details of Method.

The electrodes are each $4\frac{1}{4}$ inches square and $\frac{1}{2}$ inch thick. When yarn is under test it is wound in a single layer round the upper of each pair of electrodes. By winding the yarn in a machine fitted with a traversing mechanism set so that neighbouring threads are wound almost to touch each other, measurable conductances are obtained. The electrodes are fitted with lugs for gripping them in the machine and their edges are rounded so as not to cut the yarn. The face of each electrode in contact with the yarn is highly polished and optically flat. This contact is improved by placing weights on the upper electrode.

## Electrical Circuit.

The practical details of the simple circuit used for the measurements are shown in Fig. 1.

In Fig. 1 E and E′ are the electrodes. G is an Ayrton Mather galvanometer ; S a shunt, serving also as a key ; P is a Pohl commutator ; and C accumulators resting on a glass plate supported on blocks of silica. The lower electrode and one terminal of the galvanometer are earthed.

After closing the circuit the current through the galvanometer is adjusted quickly by means of the shunt to give a convenient deflection.
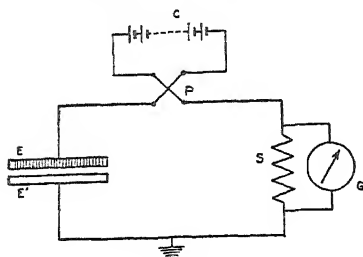


FIG. 1.

This deflection falls from its initial value and the reading is therefore taken after an arbitrary period of one minute, the direction of the current is now reversed and the deflection read again after one minute. The mean of these deflections is used to calculate the resistance.

Owing to the inherent variations in the resistance of a yarn or cloth from one portion to another it is necessary to make several determinations each on a separate portion of the sample, if a representative value of the resistance of the whole sample is desired ; but the method gives consistently reproducible results for each separate portion tested. It has been usual when comparing different yarns by this method to compare the mean transverse resistance of equal lengths of the yarn ; but the suitability of a yarn for a particular purpose will depend, of course, on other factors as well, such as covering power and mechanical properties.

## Humidity Control.

The moisture-content of a sample of silk has a very pronounced influence on its electrical resistance, a small increase in the moisture-content producing a large decrease of the resistance ; thus at 80 per cent. R.H. the resistance of a sample of silk is only 1/10th or so of its value at 75 per cent. R.H. The amount of this moisture-content depends on the relative humidity of the atmosphere with which the sample is in hygroscopic equilibrium, and it is therefore usual to study the relationship between the resistance of the sample and the relative humidity of the atmosphere in which it is present.

The earliest systematic observations recorded on this relationship for silk were made by Kujirai and Akahira,[7] who measured the transverse resistance of cloth as wound on a gold-plated cylinder and covered by gold-plated gauze. More extensive measurements were made by Murphy and Walker, who measured the longitudinal resistance of tussah and mulberry silk yarn in the manner already described.

The results given by these workers together with measurements made by the authors on spun tussah yarn are given in Fig. 2 ; here the logarithm of the resistance is plotted against the relative humidity. Although the curves allow of no
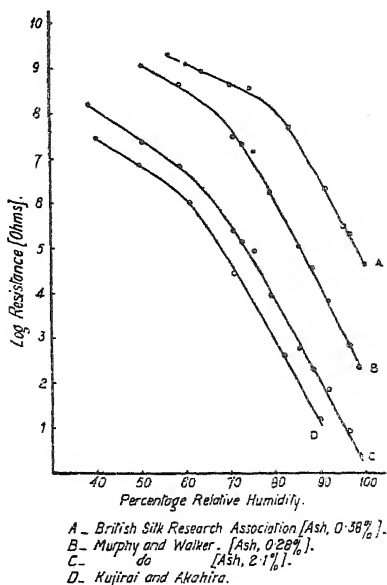


A_ British Silk Research Association [Ash, 0·58%].
B_ Murphy and Walker. [Ash, 0·28%].
C_    do     [Ash, 2·1%].
D_ Kujirai and Akahira.

FIG. 2.

comparison of the resistivities of the materials studied, their general similarity indicates that there is no essential difference between the longitudinal resistance of a spun tussah yarn as measured by Murphy and Walker and the transverse resistance of yarn or cloth as measured by the authors and Kujirai and Akahira.

It will be seen that the change of resistance with humidity is exceedingly rapid ; even on a logarithmic scale the curves fall sharply as the humidity increases. Somewhat similar results are obtained for cotton[1-4] and the other textile fibres.

The very great change in resistance with comparatively small change in humidity is the main cause of the difficulties found in studying the insulation resistance of hygroscopic materials such as textile yarns and fabrics. Considerable work was necessary before the difficulties were overcome and the experimental methods now described were sufficiently developed to make possible the accurate study of the changes in resistance of silk with electrolyte content described in the last part of this paper.

The experimental methods of humidity control finally evolved and found to be satisfactory were as follows :—

1. The experimental work at the various humidities was carried out in a small constant temperature and humidity room built inside a larger laboratory and controlled at the test humidity required. The air in this room was continuously recirculated through a large filter 18 in. square of cotton wool. This removes the specks of dust and soot normally present in the air of an industrial locality. (With a fine silk yarn the electrodes may be separated by less than 0·01 cm. and



FIG. 3.—Conditioning Box.

such soot, etc., may, with such materials, cause abnormally low resistance values, or even a short. The risk of damage to the expensive optically flat electrode faces by a short is obviated by a microfuse in the circuit.)
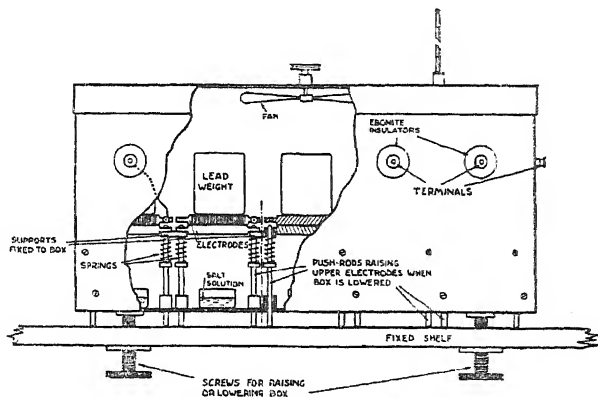
2. The effect on the test materials of the humidity ripple caused by the operation of the control mechanisms of the room was minimised by enclosing the test electrodes in boxes containing salt solutions, etc.,[5, 6] giving the same humidity as that of the control room. Fig. 3 shows diagrammatically the type of conditioning box used. It is fitted with push rods so that the upper electrodes can be raised from outside for " conditioning " the material under test and lowered again into position for test.

3. Minor fluctuations were allowed for by running blank controls together with the materials under test. The resistance of the material under test and that of the control were measured as nearly as possibly simultaneously. The use of these controls is illustrated in the experiments described in the last part of the paper. Any changes in resistance common to both samples, of whatever origin, are allowed for by such controls.

The equilibrium moisture-content or " regain " or a sample of silk at any particular humidity is somewhat less if the silk approaches this equilibrium from a lesser moisture-content than if it approaches it from a greater

moisture-content, the difference depending upon the magnitude of the humidity cycle traversed by the silk. Thus as pointed out by Murphy and Walker the relationship between resistance and relative humidity is less exact than that between resistance and moisture-content. This lack of exactitude and the great dependence of the resistance upon the moisture-content is probably responsible for some of the vagaries found in repeating resistance measurements.

## Effect of Pressure.

The resistance of a layer of threads sandwiched between two electrodes is found to decrease as the mechanical pressure exerted on the layer through the electrodes is increased, a result to be expected owing to the better contact between the threads and the electrodes, and perhaps to the flattening of the threads under the higher pressure. Fig. 4 represents the results of experiments on the change in resistance due to a cyclic increase and decrease in electrode pressure.

The load ordinarily applied in routine experiments with $4\frac{1}{4}$ inches × $4\frac{1}{4}$ inches electrodes is usually about $22\frac{1}{2}$ lbs. total weight including that of the top electrode, for 100-200 threads.



[a] Jap silk cloth [Area 60 sq.cm.]    [b] Spun Tussah yarn, 60/1. [Total length 100 x 10·5 = 1050 cm].

—— Increasing electrode pressure.    - - - - Decreasing electrode pressure.
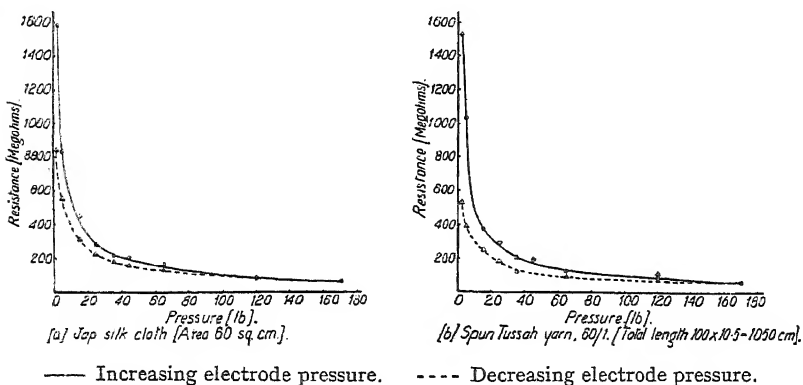
FIG. 4.

Test-voltage, 50 volts. Electrodes earthed during interval of 15 mins. between successive determinations on the same sample. 70 per cent. Relative Humidity; resistance corrected for minor variations by control determinations on samples maintained under constant pressure of 15 lbs.

## Effect of Magnitude and Duration of Test Voltage.

Within the range of humidities studied (60-100 per cent. R.H.) the test-layer of silk yarn or cloth between the electrodes shows some of the properties of an electrolytic cell. Thus the development of a back E.M.F. is indicated by the increase of the resistance during the passage of the current used in its measurement, and by the appearance of a small current in the reverse direction when the circuit is re-closed after cutting out the measurement-current. In a layer of threads of spun tussah yarn at 75 per cent. R.H. of initial resistance 5 mgoh. that had been subjected to a potential difference of 10 volts for 17 hours, this reverse current was 0·12 microamperes 15 secs. after reclosing the circuit. It fell to 0·10 m.a. in 1 min., 0·04 m.a. in 15 mins., and 0·02 m.a. in 30 mins. Within the range 75-100 per cent. R.H., test voltages of 10 to 100 volts applied for from 1 min. to 18 hours did not produce a back E.M.F. greater than 2 volts. This back E.M.F. was measured by balancing against the E.M.F. provided by a vernier potentiometer.

The increase in the resistance with time under a constant test-voltage is however much greater than can be explained by the growth of this back E.M.F., and it seems probable that the measuring current produces a change in the distribution of the electrolytes in the silk. Murphy[3] has shown that such a change occurs in threads of cotton stretched between platinum electrodes ; at high humidities a region of high resistance developed in the middle portion of the thread, whilst there was a suggestion of the formation of acid as a product of electrolysis, at the anode. In similar experiments with copper electrodes no formation of acid was observed.

Again, the fact that the observed resistance is less in general under the higher than under the lower test-voltages is a complex phenomenon which cannot be explained simply by the existence of a back E.M.F.

### Effect of Electrolytes Normally Present.

The removal of the 1-2 per cent. of inorganic matter normally present produces a very great increase in the electrical resistance of silk. In one sample of tussah silk yarn reduction of the ash from 1·59 per cent. to 0·20 per cent. by a washing treatment with acid followed by water produced a sixteen fold increase in resistance. In another yarn a somewhat similar treatment produced an increase in resistance of some four hundred times.

These measurements led to a study of the relation of the electrical resistance of silk to its amphoteric properties. Some of this work is now described.

### Study of the Relation of the Electrical Resistance of Silk to its Amphoteric Properties.

Fibroin or degummed silk is a complex insoluble amphoteric protein behaving as a base or as an acid when immersed in an aqueous solution of a salt, according to the degree to which the solution is acidic or alkaline. There is chemical evidence of the existence of a turning point in the character of silk from basic to acidic [8] in the neighbourhood of 4 on the $p_H$ scale ; minimal values of the swelling of silk occur also in the neighbourhood of $p_H$ 4 in which therefore, according to these criteria lie one or more isoelectric points. The existence of isoelectric points or of an isoelectric range has been reported at various $p_H$ values [9-16] from 1·4-5·1 as is perhaps to be expected considering the variety of methods used for the determination, and the complex constitution of silk. Some of these isoelectric points refer to mechanically disintegrated or to regenerated fibroin.

The mulberry silk (Bombyx mori) now studied was degummed and the normal foreign mineral matter was removed without apparent change in the structure of the silk. It seemed likely that the silk removed from a solution of a $p_H$ value in the neighbourhood of 4 would have the highest resistance because the chemical evidence referred to above indicated that it would then contain the least electrolyte. The necessary presence of adherent liquor in the silk removed from the solution makes a complication because the electrolyte derived from it contributes to the conductance of the silk ; this caused the investigation to be restricted to the $p_H$ range 2-9.

The earlier experiments were made on the resistance of silk yarns that had been allowed to attain equilibrium with solutions of various $p_H$ values at intervals of 1 $p_H$. They showed that samples that had attained equilibrium at $p_H$ 3·8 (taken as the isoelectric point, on chemical grounds) had a higher resistance than samples that had attained equilibrium with more acid or less acid solutions.

Cloth is simpler to handle and was therefore used in the more exact studies of the $p_H$ effect now described.

### Preparation of Material.

Squares of a size ($4\frac{1}{2}$ inches $\times$ 4 inches) convenient for the electrodes were cut from a Japanese net silk and were examined carefully. Those that contained knots, specks of foreign matter or other blemishes were rejected and the remaining squares were then weighed separately and all those that differed by more than $\pm$ 2 per cent. from the mean weight were rejected. Another portion of the cloth was cut into larger pieces and served as wrappers for the squares in all the subsequent washing, centrifuging, etc. The material was washed exhaustively in numerous successive warm baths of 1 per cent. aqueous ammonia, then in a 0·5 per cent. solution of sulphuric acid and finally exhaustively in distilled water until the $p_H$ (4·6-5·0) of a fresh quantity of the distilled water was not altered by contact with the silk.

Four series of measurements were made. In the two earlier series the silk was in equilibrium with the solutions at intervals of 1 $p_H$ unit, in series 3 the interval was 0·5 $p_H$ and in series 4, 0·2 $p_H$. In series 1 (Fig. 6) four pieces of cloth together with their wrappers were placed in each of several separate quantities of water and the $p_H$ of each quantity was adjusted by adding $N/100$ hydrochloric acid or $N/100$ sodium hydroxide from time to time until the respective solutions were in equilibrium with the silk at intervals of 1 $p_H$ from $p_H$ 2 to $p_H$ 9, except that $p_H$ 3·8 was substituted for $p_H$ 4. In series 2 (Fig. 5) the silk was placed in an aqueous solution of sodium chloride ($N/50$) instead of in water and the $p_H$ adjustment was made by adding $N/100$ hydrochloric acid or $N/100$ sodium hydroxide that was $N/50$ with respect to sodium chloride ; but otherwise the procedure was the same as in series 1.

When equilibrium was attained the squares were placed in their wrappers and centrifuged (each set of 4 squares separately) for 2 minutes at 2640 r.p.m. The squares were then conditioned at 75 per cent. R.H. in the constant humidity chamber where also the measurements were made.

Variations in the resistance caused by minor variations in the humidity chamber were compensated for by determining the resistance of one square out of each set of four from each equilibrium solution, then of a second square of each set of four and so on, the whole series of measurements being made very rapidly.

In series 3 (Fig. 7), twenty squares were caused in consecutive experiments to attain equilibrium with solutions of $p_H$ 2·3, 2·8 . . . 6·8 and were then centrifuged, conditioned, and their resistances determined. Twenty more squares were similarly treated at $p_H$ 6·8 and were used as blank controls. Squares and wrappers were immersed in a large volume of sodium chloride ($N/50$), and the $p_H$ of the solution was adjusted to the required value by adding the necessary amount of a solution of hydrochloric acid ($N/10$) or of sodium hydroxide ($N/10$) that was at the same time 1/50th normality with respect to sodium chloride. Simultaneously with each treatment of these twenty " variable " squares in solutions of different $p_H$ values, the twenty " control " squares and the wrappers were treated similarly in another solution of sodium chloride ($N/50$) (Fig. 8) but always at $p_H$ 6·8. A similar procedure was followed in series 4 except that the solutions were at 3·2, 3·4, etc., to 5·2, the solutions for the controls being at 5·2. Both variable and control squares were then centrifuged separately in their wrappers, conditioned and their resistance measured. About 3 days were required for the adjustment of each solution to a constant equilibrium $p_H$ value. The $p_H$ determinations were made colorimetrically. The $p_H$ of some of the solutions were checked electrometrically and it is believed that the colorimetric determinations were correct to within 0·1 $p_H$. In each series the resistances of the pieces of cloth were measured, first singly and then in pairs (two layers of cloth between the electrodes).

## Results.

Table I. is typical of the results obtained.  It shows the results obtained in series 4 with single pieces of cloth.  Col. 1 gives the mean resistances $(R)$ of the " control " samples $(p_H$ 5·2) and Col. 2 the mean resistance $(R_1)$ of the " variable " samples $(p_H$ 5·2 — 3·2), the values of $R$ and $R_1$ determined simultaneously being placed in the same horizontal lines.  Col. 3 gives the ratio $R_1/R$.

It will be observed that the values of $R$ in Col. I. show considerable variations although they were all determined under conditions intended to be similar, the simultaneously determined values of $R_1$ are, however, affected by corresponding variations.  Thus the pronounced maximum at $p_H$ 4·2 is regarded as a definite $p_H$ effect.  The close agreement between the values of $R$ and $R_1$

TABLE I.—MEAN RESISTANCE (MEGOHMS) OF SINGLE PIECES OF CLOTH.  SERIES 4.

| I. Control Samples, $p_H$ 5·2. | II. "Variable" Samples. | | III. |
|---|---|---|---|
| | | | $R_1/R$. |
| R. | $p_H$: | $R_1$. | |
| 175 | 5·2 | 174 | 0·99 |
| 76 | 5·0 | 104 | 1·37 |
| 118 | 4·8 | 187 | 1·58 |
| 219 | 4·6 | 332 | 1·53 |
| 67 | 4·4 | 112 | 1·67 |
| 147 | 4·2 | 475 | 3·23 |
| 80 | 4·0 | 154 | 1·93 |
| 154 | 3·8 | 201 | 1·30 |
| 157 | 3·6 | 214 | 1·36 |
| 113 | 3·4 | 115 | 1·02 |
| 259 | 3·2 | 205 | 0·79 |

in the first line of the table in which the variable and control samples have the same equilibrium $p_H$ (5·2) supports this view.  This table incidentally illustrates the usefulness of the blank control.

The results obtained in the four series are shown graphically in
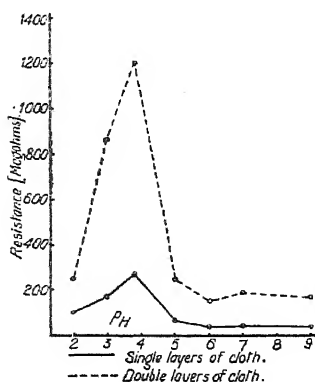


FIG. 5.  (Series 2.  Chloride.)
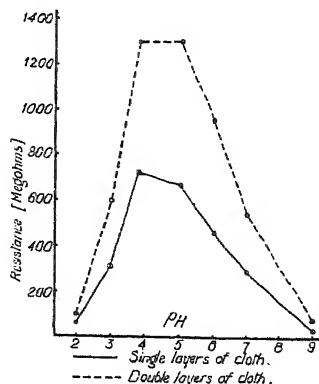


FIG. 6.  (Series 1.  Water.)

Figs. 5 to 8, in which the continuous lines refer to the measurements on single pieces of cloth and the dotted lines to those on pairs of pieces.

Comparing Fig. 5 (series 2) and Fig. 6 (series 1) it will be seen as might be expected that the maximum at $p_H$ 3·8 has been accentuated by the use of the sodium chloride.  These figures merely indicate the neighbourhood of the maximum since measurements were made only at intervals

of $1$ $p_H$. This $p_H$ $3·8$ was chosen on chemical grounds.[8] The position of the true maximum is better indicated by Figs. 7 and 8. These results show that to prepare silk of maximum resistance the solution from which the silk is finally removed should be in equilibrium with it at a $p_H$ somewhat greater than 4. The close $p_H$ intervals of series 4 suggest that this $p_H$ for maximum resistance is near $p_H$ $4·2$ but a further subdivision of the intervals might move it to $4·1$ or $4·3$.

The experimental results do not give information about the resistance of silk that has been in equilibrium with water of $p_H$ 7 free from electrolytes ; if such conditions were attainable the silk would presumably be of high electrical resistance owing to the absence of electrolytes. All the experimental results refer to silk containing electrolytes because even in series 1 the distilled water used was not neutral and the neutral point was attained by the addition of alkali. Moreover although "ash-free" silk was used it contained traces of mineral matter (ash $0·04$ per cent.)
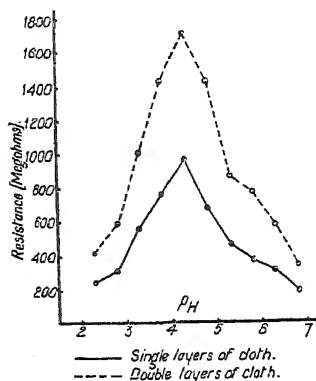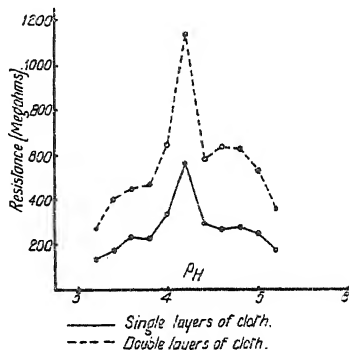


FIG. 7. (Series 3 )    FIG. 8. (Series 4.)

## Effect of Adherent Liquor. Isoelectric Point.

When the resistance of the silk is being measured the silk is no longer in the same condition as it was in the equilibrium solution ; during centrifuging some water is lost by evaporation apart from the water in the expressed liquor, and changes in the moisture-content occur subsequently during conditioning. The total conductance of the silk at the time of measurement has thus a component contributed by the electrolyte that was fixed by the silk when in the equilibrium solution and a component contributed by the electrolyte derived from the adherent liquor. Supposing the minimum amount of electrolyte is fixed by the silk when the $p_H$ of the equilibrium solution is that of the isoelectric point, the contribution of the adherent liquor to the total electrolyte in the isoelectric silk would be rather greater than the contribution of the same amount of adherent liquor to the total electrolyte in silk that had been in equilibrium with a solution of higher $p_H$ than that of the isoelectric point, because although the salt concentration of the solution is constant the acid concentration is of course slightly less in the solution of higher $p_H$. Thus if this variation in the amount of the electrolyte contributed by the adherent liquor near the isoelectric point is sufficient to affect the measured resistance of the silk it will tend to

make the solution $p_H$ for maximum resistance somewhat greater than the isoelectric point, and if $p_H$ 4·2 gives the true maximum of resistance, the isoelectric point will be somewhat less than this. As, however, the value $p_H$ 4·2 found for the maximum by the method described (series 4) cannot, owing to the intervals between the equilibrium $p_H$ values, be said to mean more than that this maximum lies between say $p_H$ 4·1 and $p_H$ 4·3, the variation in the composition of the adherent liquor is of the less account. After centrifuging, the silk weighs about 70 per cent. more than its dry weight. Of these 70 parts about 40 may be attributed to the imbibed liquor leaving about 30 per cent. for the adherent liquor, if loss due to evaporation is neglected. Studies of the titration curve of silk which will be the subject of a later communication indicate that only a small proportion of the total electrolyte in silk removed from a solution of low acid concentration (about $p_H$ 3) would be contributed by the acid in this amount of adherent liquor. We conclude therefore that the slope of the $p_H$-resistance curves between $p_H$ 3 and $p_H$ 4·2 is not greatly affected by variations in this contribution.

The $p_H$ value 4·2 found for the maximum resistance is intermediate between the $p_H$ values 3·8 and 4·7 of buffer solutions in which minimal values of the swelling of silk filaments were observed.[9]

Experimental studies of electrical resistance such as this may furnish an additional method of value in the determination of the probable isoelectric point of similar insoluble amphoteric substances.

### REFERENCES.

[1] Murphy and Walker, *J. Physic. Chem.*, **32**, 1761, 1928.
[2] Murphy, *ibid.*, **33**, 200, 1929.
[3] Murphy, *ibid.*, **33**, 509, 1929.
[4] Williams and Murphy, *Bell System Tech. J.*, 8, 225, 1929.
[5] Wilson, *Ind. Eng. Chem.*, **13**, 326, 1921.
[6] Adams and Merz, *ibid.*, **21**, 305, 1929.
[7] Kujirai and Akahira, *Inst. Phys. Chem. Res. Tokio*, **1**, 95, 1922-1924.
[8] Denham and Brash, *J. Text. Inst.*, **18**, Special issue, T520, 1927.
[9] Denham and Dickinson, *Trans. Faraday Soc.*, **29**, 300-305, 1933.
[10] Dumanski, A. and Dumanski, O. A., *Kolloid Z.*, **66**, 24, 1934.
[11] Elöd, *Z. angew. Chem.*, **40**, 262, 1927.
[12] Harris, *Bureau of Stand. J. Res.*, **9**, 557, 1932.
[13] Hawly, Jr., and Johnson, *Ind. Eng. Chem.*, **22**, 297, 1930.
[14] Meunier and Ray, *C.R.*, **184**, 285, 1927.
[15] Nakajina, *Chem. Abs.*, **22**, 2995, 1928.
[16] Shozo Bito, *Bull. Seri. and Silk Ind. Japan*, **4**, No. 2, 2-3, 1931.

*British Silk Research Association.*

# AN "ELECTRODELESS" METAL VAPOUR LAMP FOR THE PRODUCTION OF RESONANCE RADIATION.

By Fred Fairbrother and James L. Tuck.

Frommer and Polany[1] have shown that the rates of high velocity gas reactions between sodium vapour and organic halogen compounds may be measured by the "Life-period" method. This method[2] involves, in addition to the measurement of various temperatures and pressures, the estimation of the number of atoms of one of the reactants (in this case sodium) which are present in the reaction zone or "flame" at a stationary state of the reaction. Frommer and Polanyi accomplished this by measuring photographically the absorption of sodium resonance light by the sodium atoms in the reaction zone. Their experimental arrangement included the use of indirectly excited sodium resonance radiation produced by illuminating the plane end of a tube containing heated sodium vapour by light from a sodium arc lamp ; the details are given in their paper.

This method, however, whilst producing light of the required quality, is somehat unwieldy, requires constant attention and gives only a weak diffuse radiation.

The direct light, on the other hand, from a sodium arc or commercial type of glow-discharge lamp cannot be used, as the sodium D lines from such a source are very broad and therefore quite insufficiently absorbed by sodium vapour of low density.

For use with this method of measuring reaction velocities, we have developed a simple type of metal vapour lamp from which the sodium D radiation is very intense and at the same time very narrow, and is almost completely absorbed by a few centimetres of sodium vapour of low density.

Hasche, Polanyi and Vogt[3] have discussed the characteristics of resonance line shape and have shown that in the absence of Stark effect widening and large Doppler effects, the most marked factor in line broadening is self-absorption of the line, the extreme case of which is self-reversal of the line, which may result from a layer of unexcited vapour between the source of emission and the observer. By self-absorption, we mean that the centre of the line is diminished in relative intensity as compared with the flanks, but is still the brightest part of the line. The chief causes of this self-absorption are a thick layer and/or a high pressure, of emitting vapour.

In the lamps to be described, these causes have been overcome. The excitation of metal vapour at a very low pressure (ca. $10^{-4} - 10^{-5}$ mm.) has been obtained by means of the electrodeless discharge, by applying to the metal vapour, an alternating potential at a frequency of the order

[1] Frommer and Polanyi, *Trans. Faraday Soc.,* **30,** 519, 1934.

[2] Polanyi, *Nature,* **132,** 747, 1933.

[3] Hasche, Polanyi and Vogt, *Z. Physik,* **41,** 583, 1927.

of $10^8$ cycles per second, corresponding to a wavelength of about 3·10 metres. It is well known that at such frequencies a discharge can be maintained in a gas at a very low pressure with the added advantage, from the constructional point of view, that the only electrodes necessary may be *outside* the tube containing the gas or vapour.

Our efforts were at first directed towards the production of a more convenient source of indirectly excited resonance radiation and led to the design of the lamp shown in Fig. 1.

A is a double-walled glass vessel containing sodium vapour, surrounding one end of the resonance cell B, which also is an evacuated tube containing sodium ; the latter tube is provided with a plane end window and is independently heated along the portion X which is



FIG. 1.

outside the asbestos air-oven C in which A is electrically heated to about 200°. By this device it is possible to maintain the pressure in B at a somewhat lower value than that in A and secure at the same time an intense discharge in A and a minimum of self-absorption of the light emitted from B. The electrodes consist of coarse mesh copper gauze wound round the outsides of A and B respectively. It will be observed that since B is effectively within a Faraday cylinder, the sodium atoms within it are not excited by the high-frequency discharge but only by absorption of the resonance radiation from A which readily penetrates the coarse gauze.

Lamps were also constructed in which A was of the shape of a Dewar vessel and enclosed B, which was much shorter and was not independently heated. In this case self-absorption may be cut down by blackening the rear portion of B so that only a thin layer of sodium vapour near the window is used ; such a device however decreases the intensity of the radiation.

The radiation from such lamps, particularly if a shield is used to cut off stray light from A, contains only the resonance lines of the metal, which can be kept within fairly narrow limits by the devices indicated.



*View of Lamp tube from above.*

FIG. 2.

It was then found that the radiation from a lamp of the form shown in Fig. 2 while spectrally less pure than from the former, in that it also contains to a certain extent the secondary sodium spectrum, was nevertheless absorbed to a high degree by sodium vapour, whilst the construction and manipulation of the lamp were much simpler.

Self-absorption is here avoided by flattening the tube in the middle so that only a thin layer (ca. 2 mm.) of emitting vapour is used and by keeping the vapour pressure of the sodium low, of the order of $10^{-5}$ mm.

It may be calculated from the data given by Hasche, Polanyi and Vogt,[3] that a layer of excited sodium vapour 2 mm. thick, should produce a line of good profile, if the pressure of the sodium vapour be less than about $10^{-4}$ mm. corresponding to a temperature of about 205°. Above this temperature the relative broadening increases rapidly. On the other hand, the illumination falls off rapidly as the temperature is decreased. We have therefore operated the lamp at temperatures between 174° and 205° for the absorption measurements to be described.

The device of a flattened tube to decrease self-reversal has been used by Houtermans[4] who describes a hot-cathode lamp for the production of resonance radiation, particularly of mercury vapour. The present lamp however is much simpler in construction, contains no inert gas, and we believe, will operate at much lower vapour pressures.

The lamp is constructed as follows. A tube of suitable glass is prepared of the form as shown in Fig. 3, the only dimension of importance being the internal width of the flattened portion of B, from which the radiation is subsequently obtained: we found that this could not profitably be reduced below about 2 mm. as the discharge in narrower tubes was very irregular and the minimum pressure of metal vapour necessary for the discharge was much higher.
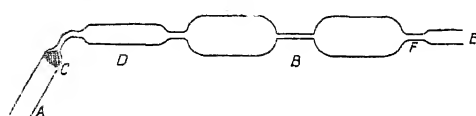


FIG. 3.

A piece of clean sodium is introduced into A and the open end sealed. The tube assembly is then attached at E with picein to a good vacuum system and evacuation commenced. The sodium in A is gently warmed, and when visible gas evolution has ceased and the pressure in the system has fallen to about $10^{-3}$ mm., a little sodium is distilled into D, and A is sealed off. (It was found that B could not be out-gassed efficiently with A attached.) The plug of copper gauze at C prevents metal or oxide from being ejected from A into D during the initial and often rather violent bubbling of the sodium.

B is then out-gassed for about 2 hours at a temperature above 300°, the progress of the evacuation being followed by the passage of the high-frequency discharge through the tube, temporary electrodes being wound round the ends of B. This out-gassing is continued until no visible discharge passes through the tube ; a discharge can be observed at pressures which are too low to be conveniently read on a McLeod guage.

B is then allowed to cool a little and sodium is distilled into it from D, a few milligrams only being sufficient ; D is then sealed off from B.

The sodium is then distilled repeatedly from end to end of B through the flattened portion, the high-frequency discharge being maintained throughout this operation. Finally B is sealed off at F. We have found that this repeated distillation of the sodium *through the discharge* is necessary in order to free the metal from hydrogen, the spectrum of which is otherwise superimposed on that of the sodium.

The design of the air oven in which the tube is heated must be such as to minimise the electrical losses : if there be much electrical damping the oscillator may cease to function. The walls of the oven, and the heater, must be at least 5 cm. from the walls of the tube and the former should preferably be made of asbestos or other non-conducting material. (We have also used tinplate boxes for this purpose, about 20 × 20 cm. and adequate length, lined with thick asbestos sheet, with a woven resistance mat at the bottom as a heater.) Copper or nickel foil electrodes are used.

[4] Houtermans, *Z. Physik*, **76**, 474, 1932.

Various kinds of glass were used for the lamp tubes. To obtain some idea of their respective suitabilities, a number of pieces of glass rod of different compositions were sealed in vacuo with a little sodium and heated. These became brown in the following order : quartz, Jena Normal glass, Jena Geräte glass and Pyrex, Soda glass. The browning was increased on passing the high-frequency discharge. Pyrex tubes were found to be quite satisfactory and only became brown slowly, provided that they were not used at too high a temperature with an intense discharge. The tubes however are so easy to prepare that their life is not a major consideration. We were also able to make, by the courtesy of the General Electric Company Ltd., Wembley, lamps of their special sodium resistant glass. These have been in prolonged use and show no browning.

A similar technique has been used to prepare quartz lamp tubes containing cadmium and thallium respectively, and glass lamps containing other alkali metals and mercury. The caesium and rubidium were prepared by substituting a mixture of the chloride of the metal in question with calcium, for the metal introduced into A (Fig. 3). Tubes filled with mercury vapour give a brilliant discharge at ordinary temperatures and emphasise the necessity for a liquid air trap between the lamp tube and a mercury vapour pump during the filling of the tube with the desired metal, unless this be mercury.

The high-frequency discharge was produced in each case by a short-wave valve oscillator working at about 3 to 10 meters—the wave-length being measured by a pair of Lecher wires and a flash-lamp bulb. Many short-wave oscillator circuits have been described in the literature of the subject, and a number were tried.



FIG. 4.

$Ch_p$, $Ch_g$ 150 turns 36 S.W.G. on a 1 cm. diameter former; $Ch_f$ 25 turns 16 S.W.G. on a 2·5 cm. diameter former; $R_1$ 25,000 ohms; $R_2$ 5000 ohms; $R_3$ 300 ohms; $C_1$, $C_2$ 0·00001$\mu$ F; $L_s$, $L_p$ single turn of 12 S.W.G. copper wire about 15 cm. diameter.

Of these, none was found to be more reliable than the simple circuit shown in Fig. 4, which is a slight modification of a well-known circuit. The values of the resistances given in the diagram refer to one particular oscillator and valve, and may be found to vary somewhat for different valves. We have several Mazda PP5/400 valves successfully in use : the grid current must be kept low and the filament run at its full rated current of 2 amperes or over, otherwise it is found that the emission falls and the oscillations cease. The arrangement adopted for automatic grid bias ensures that the valves does not fail through excessive anode current if the oscillations suddenly cease, which may occur for example, if the leads to the lamp are handled or come into contact with the metal work of other apparatus. The frequency may be varied by means of the small variable air condenser $C_1$, which must have a wide spacing between the fixed and movable plates or be operated with a larger mica dielectric condenser in series with it. The output is obtained from the tuned loop $L_s$ coupled magnetically to the primary loop $L_p$. The coupling between

these loops must not be too tight. The leads from the secondary loop to the lamp may be made quite long (*e.g.* several meters) without much loss in efficiency, although thereby the tuning and therefore the frequency are altered. The tuning of the secondary loop is fairly critical with low lamp temperatures and becomes very flat as the temperature rises. A small 5 cm. diam. bulb containing hydrogen at a low pressure or mercury vapour at room temperature serves as a convenient indicator during preliminary adjustment. The above circuit may be operated on 400 or 500 volts D.C. or A.C. (unrectified) though for some purposes the intermittent nature of the light in the latter case may be undesirable.

The results of some measurements made with a sodium lamp of the type shown in Fig. 2 appear in Figs. 5 to 7. In Fig. 5 is given the absorption (as log. $I_0/I_t$ and as per cent. absorption) of the light as a function of the temperature of the absorption cell and the calculated moles per square cm. of sodium in the path of the light. The sodium vapour used for the absorption was contained in a Jena glass tube about 3 cm.



FIG. 5.

diam. with plane ends 4·64 cm. apart. This tube was filled in much the same manner as the lamp tubes described above and was heated in a capacious electrically heated air oven to secure uniformity of temperature. Condensation of sodium on the plane ends of the tube was prevented by the inclusion of small auxiliary heaters near the ends of the tube. The temperature was measured by three calibrated thermometers alongside the tube. The absorption was measured visually by means of a Hilger Nutting Photometer, using the total un-resolved light from the lamp, corrections for the absorption by the cold cell being applied in the usual manner. The absorption tube was heated to a temperature of about 200° and allowed to cool slowly, by adjustment of the heater currents, over a period of several hours whilst observations were made. The measurements at absorptions over 90 per cent. were very difficult owing to the low residual illumination, but readings by several observers agreed very closely. The vapour pressure of the sodium and the resultant number of moles of sodium per unit area in the path of the light, were calculated from the observed temperature and the data of Ladenburg and Thiele [5] extrapolated to the required region. The absorptions are given for comparison, at two temperatures of the lamp, namely 174° (A) and 205° (B) together with a curve (C) calculated from that given by Frommer and Polanyi [1] allowing for the difference

[5] Ladenburg and Thiele, *Z. physik. Chem.*, **7B**, 161, 1930.

in abscissæ units, and (D) a curve showing a similar set of measurements to those described above, which were made with a commercial small sodium glow discharge lamp. These absorption measurements also agreed very closely with another set made by Mr. E. Warhurst with the same absorption cell and a similar lamp, using the photographic method described by Frommer and Polanyi.[1] It will be observed that the new lamp gives a much more absorbable light than the other methods, even though the spectrum contains also the secondary spectrum in low intensity: in other



$log_{10} \frac{I_o}{I}$

Lamp Temperature.

FIG. 6.

words, the absorption is limited more by the width of the resonance lines than by the spectral impurity of the secondary spectrum.

In Fig. 6 is shown the change in absorption of the light with increasing lamp temperature, in more detail. For this purpose the absorption cell was maintained at a constant temperature of 162·5°, and the temperature of the lamp varied. The extent to which the light is absorbed by a given mass of sodium vapour decreases with rise in temperature of the lamp. This is to be ascribed chiefly to the broadening of the resonance lines as a consequence of the increased vapour pressure, and only to a small degree to the increase in brilliance of the secondary spectrum.



Milli-lumens from one flat surface of lamp.

Lamp Temperature.

FIG. 7.

At all temperatures at which the lamp will operate it may be easily observed, visually, with the aid of a small bulb filled with sodium vapour at room temperature, that the light from the wide cylindrical ends of the lamp is much less absorbed by a given mass of sodium vapour than the light from the flattened portion.

In Fig. 7 is shown the change in total light output as a function of the temperature of the lamp. This curve was obtained by means of a Weston Photronic cell which possesses a maximum sensitivity in the

yellow region of the spectrum. The ordinates, milli-lumens emitted from one side of the flattened portion, are only approximate, but they are comparable : they were obtained from the published sensitivity curve of the photronic cell and the observed galvanometer readings.

The discharge first occurs visibly at a temperature of about $160^0$ which corresponds to a sodium pressure of about $1 \cdot 1 \times 10^{-5}$ mm. The discharge begins at a lower temperature if the lamp contains a trace of hydrogen ; in fact we have been able to observe the characteristic yellow sodium light in a bulb at room temperature containing sodium which had not been completely freed from hydrogen. The curve shows that the total light output increases rapidly with temperature. If the latter be further increased, the glow suddenly decreases in consequence of the damping effect of the lamp as a shunt resistance across the secondary loop ; this was observed to occur with a particular oscillator at about $250^{\circ}$.

The lamps described above are so cheap and easy to construct and operate that it is expected that they will find many other uses in the laboratory, than the one for which they were primarily designed. For some purposes, such as polarimetry and refractometry, where self-absorption is relatively unimportant, the flattening may be found to be unnecessary, and the lamp may consist of a simple tube or one which has a somewhat narrower middle portion to concentrate the discharge.

## Summary.

Metal vapour lamps are described, which are operated by means of the high-frequency discharge. Two types of lamp are described, the first for the production of indirectly excited resonance radiation and the second for the production of directly emitted radiation.

The chief features of the second type of lamp are (1) the emission of radiation, which in the case of resonance lines is not self-absorbed to any appreciable extent, this being secured by the use of a low pressure and a thin layer of metal vapour, (2) ease of construction and manipulation, no sealed-in electrodes being necessary, (3) wide applicability : *e.g.* alkali metals, mercury, cadmium and thallium have been used.

Measurements are given of the absorption of the resonance radiation from such a lamp containing sodium, and of the change in intensity and character of the light with increase in temperature of the lamp.

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# THE "PROBABILITY" OF CORROSION.

By R. B. Mears and U. R. Evans.

The *probability* of corrosion developing on a small area is controlled by laws quite different from those governing the " conditional *velocity* " (the average velocity measured in cases where attack occurs at all). The authors [1] have already found that one factor (oxygen-concentration) may shift " probability " and " conditional velocity " in different directions. From the purely scientific standpoint, measurements of probability, which give information regarding the mechanism of breakdown of passivity, are as important as measurements of velocity, which indicate the mechanism maintaining the attack. From the practical standpoint, also, probability has importance ; [2] it may, indeed, be more important to know whether—at a microscopic pore in a protective coat—corrosion is likely to occur at all than to know how quickly it will develop.

The measurements recorded below, however, are concerned with the pure-science aspect, and seek to establish the influence of sixteen " external factors " upon (*a*) the *Probability* of attack developing and (*b*) the early value of the *Conditional Velocity*, as measured over a 22-hour period. In each series of experiments, *all the factors except one* were kept constant, thus isolating the effect of varying this one factor. The external factors studied were :—

I. The Time of duration of the experiment.
II. The Area of metal exposed to the liquid.
III. The Oxygen-concentration in the atmosphere during the experiment.
IV. The quality of Distilled Water.
V. The Time of pre-exposure (to dried air).
VI. The Temperature of the experiment.
VII. The Temperature of pre-exposure.
VIII. The concentration of Salt used (potassium chloride).
IX. The effect of Anion (comparison with other potassium salts).
X. The concentration of Inhibitor (potassium carbonate in mixtures with potassium chloride).
XI. The effect of other Inhibitors.
XII. The effect of additions of Acid or Alkali.
XIII. The effect of Sulphur Dioxide or Carbon Dioxide in the gas-phase.
XIV. The nature of abrasive treatment and preliminary washing with various liquids.
XV. The character of the Scratch line.
XVI. The effect of corrosion in the neighbourhood (protective action of a recent scratch-line for a less recent one).

[1] U. R. Evans and R. B. Mears, *Proc. Roy. Soc.*, **146A,** 153, 1934.
[2] U. R. Evans, R. B. Mears and P. Queneau, *Engineering*, **136,** 689, 1933.

Some information has been obtained as to the effect of the purity of the metallic phase,[3] but "internal factors" (*e.g.* the effect of each impurity) will be studied systematically in a subsequent research.

## Materials.

The materials used were in sheet form consisting of :—

(a) **Carbonyl Iron** (K-34) of German origin ; this is nearly pure iron with a trace of carbon, generally stated to be present as carbon monoxide, although observations by W. J. Müller [4] suggest that it is present as free carbon. (Thickness, 0·35 mm.)

(b) **Electrolytic Iron**, (E-33), containing 0·06 per cent. carbon, no manganese, 0·03 per cent. silicon, 0·003 per cent. sulphur and 0·017 per cent. phosphorus. (Thickness, 0·35 mm.)

(c) **Mild Steel**, (H-33), containing 0·10 per cent. carbon, 0·39 per cent. manganese, 0·05 per cent. silicon, 0·005 per cent. sulphur and 0·03 per cent. phosphorus. (Thickness, 0·33 mm.)

(d) **Mild Steel**, (B-32), containing 0·108 per cent. carbon, 0·40 per cent. manganese, 0·062 per cent. sulphur and 0·039 per cent. phosphorus. (Thickness, 0·28 mm.)

(e) **Mild Steel**, (C-10), containing 0·21 per cent. carbon, 0·62 per cent. manganese, 0·037 per cent. sulphur, 0·042 per cent. phosphorus and 0·030 per cent. copper. (Thickness, 0·72 mm.)

(f) **Mild Steel**, (S-33), containing 0·16 per cent. carbon, 0·67 per cent. manganese, 0·27 per cent. silicon, 0·011 per cent. sulphur, 0·017 per cent. phosphorus and 0·13 per cent. nickel. (Thickness, 0·33 mm.)

Materials (b), (c) and (f) were very kindly provided by Dr. W. H. Hatfield and steel (d) by Captain Leighton-Davies.

The materials were cut into pieces $2 \times 1$ inches, which were "shuffled," four being selected at random for each experiment.

**Surface Preparation.**—Except in series 14 (where numerous methods were compared), two methods of preparing the surface were used :—

(*a*) Grinding with No. 3 (Hubert) emery paper, washing twice in carbon tetrachloride, and a final light grinding with No. 3 paper.

(*b*) Grinding with "No. 149-FF Fine" carborundum block (no paper or glue involved), washing twice in carbon tetrachloride, and a final light grinding with the block. Between preparation and the *experiment proper* all specimens underwent a definite period of *pre-exposure* in a desiccator placed in the thermostat.

## Experimental Methods.

(i) **"Square Drop Method."** This resembled the procedure used previously by the authors.[5] On the weighed specimens, two series of wax lines, 2 mm. wide, were ruled at right angles by means of a fine brush wetted with a 5 per cent. solution of paraffin wax in carbon tetrachloride, so as to give on each specimen a "chessboard" of (usually) 27 unwaxed squares each 3 mm. $\times$ 3 mm. Usually four such specimens were attached by paraffin wax to a wax-coated glass plate ; this was placed in a glass vessel of capacity 750 c.c., which was three times exhausted and filled with the gas-mixture required. Then the liquid saturated with the gas mixture under consideration was introduced and immediately run out again, leaving the square drops (usually 108 in number) on the metal. The number of drops producing rust was noted after the required "period of the experiment" ; after removal of rust by the cathodic treatment in citric acid previously used,[6] the distribution of etching within each drop was noted,

[3] Some numbers for five materials are quoted by S. C. Britton, *Nature*, **134**, 278, 1934.

[4] W. J. Müller, *Zeitsch. Electrochem.*, **40**, 124, 1934.

[5] U. R. Evans and R. B. Mears, *Proc. Royal Soc.* **146A**, 164, 1934.

[6] U. R. Evans and T. P. Hoar, *Proc. Royal Soc.* **137A**, 346, 1932.

and the number of drops affected verified. After removal of wax with carbon tetra-chloride, the loss of weight was measured.

This method was employed in Series, I., II., III., IV., VI., VII., VIII., IX., X., XI., XII., XIII., and XIV. It was not suitable for short pre-exposures and for certain other purposes; consequently, the following alternative method was adopted in Series V., XV. and XVI. (also for part of Series I.) :—

(ii) The Scratch-line Method.—Here the specimens were divided by wax lines into cells 5 by 16 mm., and in each cell a scratch 12 mm. long was made by means of a machine constructed by Mr. Ward and described elsewhere.[7] The net load was 400 grams, except in series XV, and a new H.M.V. " loud " needle was used for each scratch.

Except in those series where time or temperature were the variables under study, the standard " pre-exposure " (between preparation and experiment) was one hour in dried air at 25° C., whilst the " experiment " proper lasted 22 hours at 25° C.

## Reproducibility.

The very fact that some drops produce corrosion and others do not, indicates that the phenomenon for these small areas is essentially irreproducible. Nevertheless, a comparison between the four specimens tested in each experiment is important as showing whether the " peculiar points "—which favour attack—are distributed uniformly throughout different parts of the sheet from which the four specimens were cut. Usually the numbers for each of the four specimens show divergence from the mean value, pointing to some segregation, especially in iron E-33.

Estimates of the half-chance error, $\Delta \bar{X}$, of the " probability " numbers from the true value (the average of an infinite number of observations) based on the equation $\Delta \bar{X} = \dfrac{0 \cdot 67\ S}{\sqrt{n-1}}$, where $S$ is the standard deviation and $n$ the number of specimens, show that for K-34 (the material mainly used), there is a " half chance " that the deviations from the " true value " do not exceed 4·8 drops per set of 108 drops (or 5·2 drops, if we exclude the cases where all or none of the drops corroded on any one of the four samples; opinion may differ as to whether such cases ought to be included). These " half-chance errors " compare favourably with those of other scientific corrosion researches.

For H-33, the half-chance errors are smaller, namely 2·0 and 2·8 drops per set of specimens, whereas on E-33 they are 6·0 and 9·2 per set. There is other evidence that H-33 is the most uniform material, but unfortunately the supply was limited; efforts to obtain large supplies of more suitable material have failed, in spite of much help from metallurgical centres.

In cases where the relation between the number of drops causing corrosion left the conclusion in doubt, sets of eight specimens were used.

## Series I. Time of Experiment.

In preliminary experiments, the number of drops affected increased slowly with time, rather suggesting that the immunity of the metal below the other drops was merely due to a long induction-period. When the results of Series III. became available, they showed the increase to be accounted for by the consumption of oxygen. Special experiments, made by the scratch method in an apparatus where the oxygen consumed was replenished continuously, showed that very few drops which had not developed corrosion within fifteen minutes did so within 64 hours. This agrees with previous statistical results on corrosion at contacts with glass [8] and was confirmed by experiments on square drops lasting for 12 days.

[7] R. B. Mears and E. D. Ward, *J. Soc. Chem. Ind.*, **53**, 382T, 1934.
[8] R. B. Mears and U. R. Evans, *Trans. Faraday Soc.*, **30**, 421, 1934.

Evidently probability is approximately independent of time. The time-corrosion curve (Fig. 1) obtained by the square drop method (without replenishment) was nearly straight for 32 days, showing that, under these particular conditions, corrosion velocity is also independent of time. As indicated by Vernon,[9] Bengough,[10] Passano,[11] and others, this is not true of all conditions.
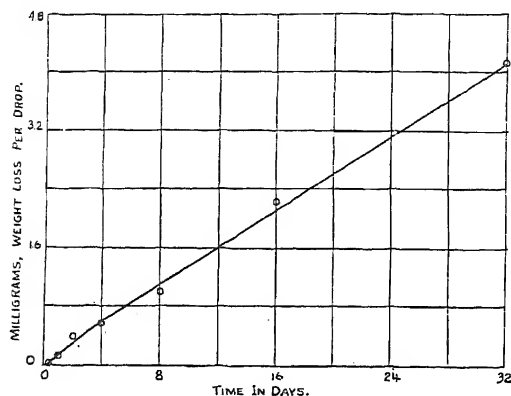


FIG. 1.

## Series II.   Area Exposed to Liquid.

Experiments with square drops of different sizes were conducted in pure oxygen on carbonyl iron and wrought iron using 0·0005 $M$. potassium chloride and pure water respectively. As shown in Table I., an increase of exposed area materially raises both the probability and the conditional velocity. In judging the figures, it must be remembered that the depth around the edges is smaller than elsewhere, and that this affects the small drops more than the large ones.

TABLE I.   (SERIES II.).

| Material. | Exposed Area, sq. mm. | Probability, Per Cent. | Cond. Velocity (mg. per Drop Corroding). |
|---|---|---|---|
| Carbonyl Iron | 1 | 5 | 0·07 |
| (FF 149 Carborundum) | 9 | 32 | 0·17 |
|  | 169 | 100 | 1·83 |
| Wrought Iron | 1 | 35 | — |
| (Milled Surface) | 9 | 94 | — |

## Series III.   Effect of Oxygen Concentration (in Oxygen-Nitrogen Mixtures).

The previous research had shown that for one material (electrolytic iron) and one liquid (0·001 $M$. potassium chloride), the probability diminishes and conditional velocity increases with the oxygen-concentration. New experiments show that this is equally true of other materials (steels H-33 and C-10) and also for carbonyl iron in distilled water. Some typical curves are given in Fig. 2 for electrolytic-iron, and steels H-33, C-10 and S-33 prepared by abrasion with No. 3 emery paper and tested by the square drop method using 0·001 $M$. potassium chloride. The only exception is steel S-33, where the probability remains at about 100 per cent., even in pure oxygen. Particularly interesting are the curves for carbonyl iron in pure water (Fig. 3), where the probability is approximately nil in pure oxygen, and approximately 100 per cent. in pure nitrogen, although in that gas the actual attack is naturally very feeble. The " corrosion-

[9] W. H. J. Vernon, *Trans. Faraday Soc.*, **19**, 840, 1924.
[10] G. D. Bengough, *J. Soc. Chem. Ind.*, **52**, 205, 1933.
[11] R. F. Passano, *Industrial and Eng. Chem.*, **25**, 1249, 1933.

expectation '' (the product of the probability and conditional velocity) is maximal at about 92 per cent. nitrogen.

## Series IV.  Effect of Distilled Water.

The special distilled water used throughout this research was obtained by boiling the ordinary laboratory distilled water for 30 minutes with alkaline
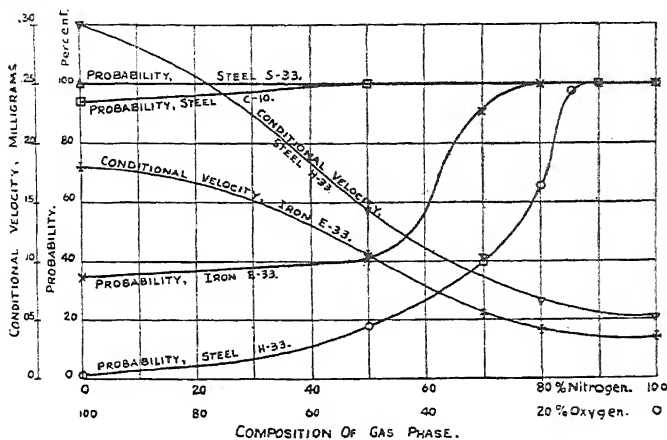


FIG. 2.

potassium permanganate and then distilling in a closed system, condensing in quartz and collecting in hard glass.   This water, tested on three different occasions on carbonyl iron in an atmosphere of 20 per cent. oxygen, 80 per cent. nitrogen gave consistent results, the probability figures being 32 per cent. 31 per cent. and 27 per cent. ;  tested after an hour's additional boiling in hard glass it still gave 30 per cent., but boiling with tin for
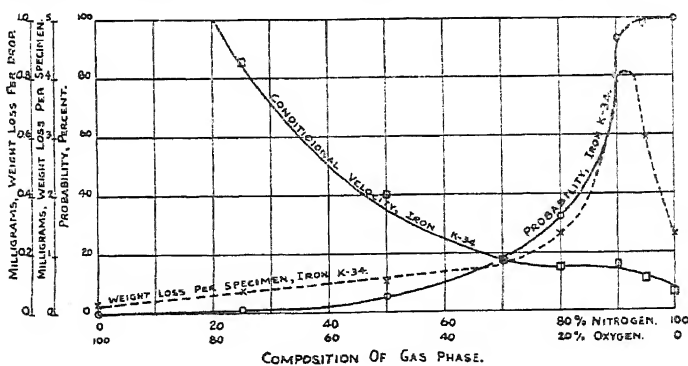


FIG. 3.

1 hour, increased the figure to 40 per cent.   Freshly distilled water condensed in tin in the Laboratory of Physical Chemistry gave high values, 69 per cent. and 80 per cent. in two tests.   The water supplied from a large still in the Chemical Laboratory (condensed in copper-nickel alloy tubes, run through tin-alloy composition pipes and stored in slate vessels) gave lower probability values (10 per cent.) but a higher conditional velocity (0·45 mg. per drop against 0·20 and 0·22 for the quartz-condensed water). Similar low probabilities (10 per cent.) and high conditional velocities

(0·40 mg. per drop) were obtained from some tin-condensed water prepared in the Laboratory of Physical Chemistry which had been stored in tin vessels for some months.   Later experiments (Series X) suggest the combination of low probability and high conditional velocity to be typical of an " inhibitor " ;  some nitrogeneous organic body was certainly present in the ordinary laboratory supply, since boiling with the alkaline permanganate produced an ammoniacal odour.

Qualitative experiments with the quartz-condensed water showed that all drops causing visible corrosion contained ferrous as well as ferric compounds, whereas those causing no corrosion showed a trace of ferric but no ferrous iron at all.   This suggests that the first product is ferrous hydroxide which is later converted to the less soluble ferric hydroxide. Where this second change occurs in physical contact with the metal, stifling of the attack will occur and no ferrous iron will be detected in the drop.

### Series V.   Time of Pre-exposure to Dried Air.

It is generally recognised that " passivating agents," like potassium chromate, will produce immunity even on freshly abraded metal, whilst " activating agents," like potassium chloride, will usually attack ordinary iron even after long pre-exposure to air.   When the liquid used is on the border-line between the activating and passivating classes, pre-exposure may be expected to influence the decision, and it is known that the invisible " air-formed film " on iron, although less important than on stainless steel, does undoubtedly influence the results in special cases.[12]   Experiments with the scratch-line method, using 0·07 $M$. sodium bicarbonate as the liquid and an atmosphere of 100 per cent. oxygen, gave the results recorded in Table IV.   Here the effect of pre-exposure is marked.   Only intermediate concentrations of sodium bicarbonate brought out this effect of pre-exposure ;  very dilute solutions (0·0005 M. sodium bicarbonate) gave 100 per cent. probability even after one week's pre-exposure, whilst concentrated solutions (0·5 $M$.) gave immunity below every drop even when applied 15 seconds after scratching.

**Series V.    Time of Pre-exposure to Dried Air.**

TABLE IV.

| Period of Pre-exposure to Dried Air. | Probability. |
|---|---|
| 0·25 minutes | 84 per cent. |
| 2      ,, | 63     ,, |
| 16     ,, | 58     ,, |
| 128    ,, | 48     ,, |
| 1024   ,, | 27     ,, |

### Series VI.   Temperature of Experiment.

Experiments on carbonyl iron with 0·0005 $M$. potassium chloride in 100 per cent. oxygen, showed that rise of temperature has a decided effect both on the probability and on the conditional velocity.   Results are given in Table V.

### Series VII.   Temperature of Pre-exposure.

In view of Vernon's results [13] on copper and brass the temperature of pre-exposure seemed of special interest.   The results recorded in Table VI.,

[12] H. Freundlich, G. Patscheke, H. Zöcher, *Z. physik. Chem.*, **128**, 321, 1927. W. H. J. Vernon, *Trans. Faraday Soc.*, **23**, 150, 1927.   W. J. Müller, *Z. physik. Chem.*, **161A**, 411, 1932.   U. R. Evans, *J. Chem. Soc.*, 1030, 1927.   S. C. Britton and U. R. Evans, *Trans. Electrochem. Soc.*, **61**, 444, 1932.

[13] W. H. J. Vernon, *Trans. Faraday Soc.*, **23**, 130, 1927 ;  *J. Chem. Soc.*, **128**, 2273, 1926.

obtained from carbonyl iron, in an atmosphere of 100 per cent. oxygen and 0·0005 M. potassium chloride with pre-exposure for one hour to dried air, indicate an enhanced probability when the pre-exposure was at 0° C. Vernon's effect was thus realised in the range 0-12° C., but not at higher temperatures ; conditions more favourable to his effect could be envisaged, but would introduce experimental difficulties.

| Series VI.   Temperature of Experiment. | Series VII:   Temperature of Pre-exposure: |
| --- | --- |
| TABLE V. | TABLE VI. |

| Temperature ° C. | Probability, Per Cent. | Cond. Velocity (mg. per Drop Corroding). | Temperature of Pre-exposure, 0° C. | Probability, Per Cent. |
| --- | --- | --- | --- | --- |
| 0 | 0 | " indeterminate " | | |
| 12 | 21 | 0·11 | 0 | 70 |
| 25 | 32 | 0·17 | 12 | 32 |
| | | | 25 | 35 |
| | | | 100 | 37 |

## Series VIII.   Concentration of Salt.

The effect of potassium chloride at different concentrations on steel H-33 below an atmosphere of purified air, using potassium chloride of different concentrations, is shown in Fig. 4.   The conditional velocity first rises with concentration, and then falls again.   A curve of similar shape



CONCENTRATION OF POTASSIUM CHLORIDE SOLUTION.
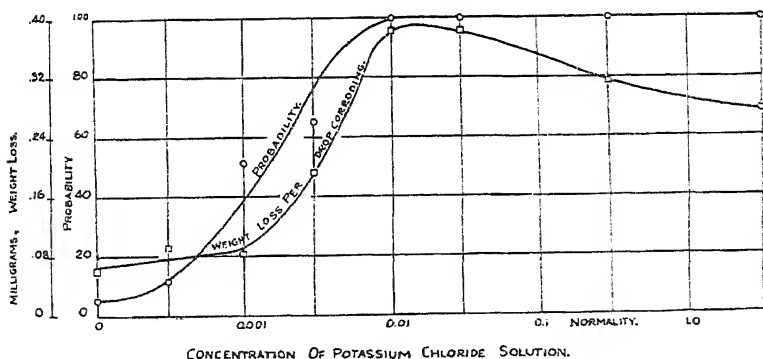
FIG. 4.

but with a maximum at a higher concentration was found from previous work [14] on half-immersed specimens.   The probability also rises with the concentration reaching 100 per cent. at 0·01 M. and maintaining this value up to the highest concentration tested (3 molar).

## Series IX.   Effect of Anion.

Comparative experiments on carbonyl iron, in an atmosphere of purified air and various potassium salts, gave results shown in Table VII. ; potassium sulphate was tested twice, so as to compare equimolecular, as well as equivalent, concentrations.   In both cases, the sulphate rather surprisingly gave higher probabilities than chlorides, but lower conditional velocities as measured by the weight-loss per drop corroding.   However, the fraction

[14] U. R. Evans and T. P. Hoar, *Proc. Roy. Soc.*, **137A**, 350, 1932.

of the drop area attacked was always smaller in the case of the sulphate solutions ; this may explain why the sulphate always gave much lower values than the chloride in leakage current experiments on aluminium made by Britton and one of the authors, and also by Tronstad and Bommen.[15] Evidently, certain views previously expressed [16] regarding ionic penetrating powers require revision.

Series IXa: Effect of Anion.

TABLE VII.

| Solution. | Probability, Per Cent. | Cond. Velocity (mg. per Drop Corroding). |
|---|---|---|
| 0·001 $M$. potassium chloride  . | 93 | 0·18 |
| 0·001 $M$. potassium iodide     . | 68 | 0·15 |
| 0·001 $M$. potassium nitrate    . | 60 | 0·15 |
| 0·001 $M$. potassium sulphate   . | 100 | 0·16 |
| 0·0005 $M$. potassium sulphate | 99 | 0·11 |

Series IXb:    Effect of Anion in Overcoming Inhibition.

TABLE VIII.

| Solution. | Probability, Per Cent. | Cond. Velocity (mg. per Drop Corroding). |
|---|---|---|
| 0·0025 $M$. potassium carbonate }<br>0·001 $M$. potassium chloride  . } | 50 | 0·12 |
| 0·0025 $M$. potassium carbonate }<br>0·001 $M$. potassium iodide     . } | 32 | 0·03 |
| 0·0025 $M$. potassium carbonate }<br>0·001 $M$. potassium nitrate    . } | 35 | 0·10 |
| 0·0025 $M$. potassium carbonate }<br>0·001 $M$. potassium sulphate  . } | 84 | 0·08 |
| 0·0025 $M$. potassium carbonate }<br>0·0005 $M$. potassium sulphate . } | 81 | 0·07 |

The effect of different anions in overcoming the inhibitive action of 0·0025 $M$. potassium carbonate is shown in Table VIII. Here again the sulphate ion is most effective, as judged by the number of points attacked.    The attacked areas remain, however, extremely localised in sulphate solutions, so that the conditional velocity as measured by the weight loss per drop corroding is again lower for the sulphate solutions than for chloride solutions.

## Series X.    Concentration of Inhibitor in the Presence of a Standard Concentration of Potassium Chloride.

Experiments on carbonyl iron in 10 per cent. oxygen and on steel in purified air using 0·001 $M$. potassium chloride containing various amounts of potassium carbonate gave results shown in Table IX.    Here small amounts of potassium carbonate increased the probability while large amounts depressed it.    On the steel the corrosion extended over nearly the whole area, but on the iron it remained very localised.    The intensity of corrosion (attack per unit area affected) tends to rise with the concentration of inhibitor.    On the steel, the conditional velocity (which is here proportional to the intensity) rises as the inhibitor-concentration is increased. This fall in probability and rise in conditional velocity were also met with in the case of potassium hydroxide (Series XII.) and oxygen (Series III.). Apparently oxygen stands on a similar theoretical footing to recognised

[15] S. C. Britton and U. R. Evans, *J. Chem. Soc.*, 1773, 1930.  L. Tronstad and B. W. Bommen, *Det Kongelige Norske Videnskabers Selskab, Forhandlinger*, **5**, 176, 1933.
[16] T. P. Hoar and U. R. Evans, *J. Iron and Steel Inst.*, **126**, 387, 1932.

Series X. Concentration of Inhibitor in the Presence of a Standard Concentration of Potassium Chloride.

TABLE IX.

| Material | Atmosphere. | Solution. | Probability, Per Cent. | Intensity (mg. per sq. mm. of Area Affected). | Cond. Velocity (mg. per Drop Corroding). |
|---|---|---|---|---|---|
| Carbonyl iron | 90 per cent. Nitrogen + 10 per cent. Oxygen | 0·001 $M$. Potassium chloride | 89 | 0·023 | 0·20 |
| ,, | ,, | 0·001 $M$. Potassium chloride + 0·001 $M$. Potassium carbonate | 99 | 0·019 | 0·14 |
| ,, | ,, | 0·0025 $M$. ,, ,, | 71 | 0·024 | 0·08 |
| ,, | ,, | 0·005 ,, ,, | 33 | 0·034 | 0·11 |
| ,, | ,, | 0·010 ,, ,, | 7 | 0·044 | 0·09 |
| ,, | ,, | 0·025 ,, ,, | 0 | Indeterminate | Indeterminate |
| Steel (H. 33) | Purified Air | 0·001 $M$. Potassium chloride + 0·0005 $M$. Potassium carbonate | 51 | 0·013 | 0·11 |
| ,, | ,, | ,, ,, | 58 | 0·015 | 0·13 |
| ,, | ,, | 0·005 ,, ,, | 74 | 0·020 | 0·16 |
| ,, | ,, | 0·0075 ,, ,, | 17 | — | |
| ,, | ,, | 0·0125 ,, ,, | 2 | 0·075 | 0·31 |
| ,, | ,, | 0·025 ,, ,, | 0 | Indeterminate | Indeterminate |

inhibitors, although it possesses no practical value owing to its limited solubility and the fact that it is consumed during the corrosion-process and also absorbed by the ferrous corrosion-products.

It seemed interesting to compare the inhibitive power of oxygen and potassium carbonate. As a basis, experiments on carbonyl iron, using 0·001 $M$. potassium chloride in an atmosphere of 10 per cent. oxygen, 90 per cent. nitrogen, were employed (experiments with 0 per cent. oxygen would have been unsuitable, since the corrosion is here probably of the hydrogen evolution type). These experiments gave a probability of 89 per cent. Raising the oxygen-concentration to 100 per cent. depressed the probability to 71 per cent. Keeping the oxygen-concentration at 10 per cent., it was found necessary to add 0·0025 $M$. potassium carbonate in order to depress the probability to the same value. Calculations based on the solubility of oxygen suggest that the inhibiting power of oxygen under these conditions is nearly twice that of potassium carbonate.

Series XI. Comparison of Inhibitors added to a Standard Solution of Potassium Chloride.

TABLE X.

| Solution. | Probability, Per Cent. |
|---|---|
| 0·001 $M$. potassium chloride . . . | 52 |
| 0·001 $M$. potassium chloride . . $\}$ 0·0075 $M$. potassium carbonate . | 18 |
| 0·001 $M$. potassium chloride . . $\}$ 0·0075 $M$. dipotassium hydrogen phosphate | 5 |
| 0·001 $M$. potassium chloride . . $\}$ 0·0075 $M$. potassium chromate . | 0 |

Series XI. Comparison of Inhibitors added to a Standard Solution of Potassium Chloride.

The results shown in Table X. were obtained on steel H-33 and 0·001 $M$. potassium chloride solution containing different inhibitors at 0·0075 $M$

concentration in purified air. Evidently potassium chromate is the most powerful inhibitor, as indicated in previous work.[17]

### Series XII. Additions of Acid or Alkali.

Experiments on carbonyl iron in an atmosphere of purified oxygen, using potassium chloride made acid or alkaline with hydrochloric acid or potassium hydroxide, gave results shown in Fig. 5. Naturally each addition affected not only the $p_H$ value, but also the concentration ; additional potassium chloride produced precisely the same increase in probability as the equivalent addition of hydrochloric acid. Additions of potassium
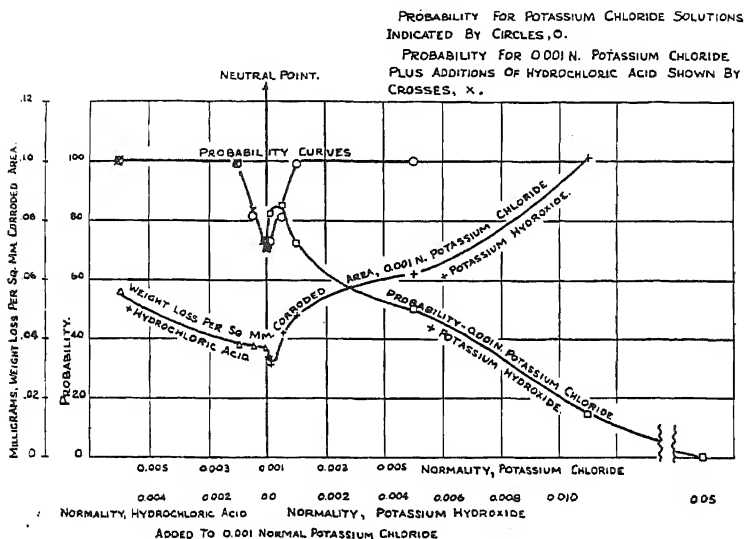


FIG. 5.

hydroxide first stimulated the probability and then depressed it, thus showing an analogy with potassium carbonate. There is a considerable range over which the $p_H$ value, *as such*, exercises comparatively little influence on the probability. The measurements of velocity show general correlation with the results of Whitman, Russell and Altieri,[18] Morris,[19] and Bryan.[20] The fact that the probability can lie far below 100 per cent. even in definitely acid solutions has industrial importance.

### Series XIII. Effect of Sulphur Dioxide or Carbon Dioxide in the Gas-phase.

Experiments using quartz condensed water on steel H-33 below various atmospheres gave the results shown in Table XI. Evidently a relatively large amount of carbon dioxide exerts little influence on the corrosion probability, although it doubles the conditional velocity. Sulphur dioxide enormously increases both the probability and conditional velocity.

[17] U. R. Evans, *J. Soc. Chem. Ind.*, 46, 1031, 1927.
[18] G. W. Whitman, R. P. Russell, and V. J. Altieri, *Ind. and Eng. Chem.*, 16, 665, 1924.
[19] T. N. Morris, *Report of Food Investigation Board*, 110 and 119, 1930.
[20] J. M. Bryan, *Trans. Faraday Soc.*, 29, 1199, 1933.

Series XIII.  Effect of Sulphur Dioxide or Carbon Dioxide in the Gas-phase.

TABLE XI.

| Atmosphere. | Probability, Per Cent. | Cond. Velocity (mg. per Drop Corroding). |
|---|---|---|
| 80 per cent. nitrogen, 20 per cent. oxygen | 5 | 0·06 |
| 79 per cent. nitrogen, 20 per cent. oxygen, 1 per cent. carbon dioxide . . . | 6 | 0·12 |
| 79 per cent. nitrogen, 20 per cent. oxygen, 1 per cent. sulphur dioxide . . . | 100 | 1·56 |

## Series XIV.  Nature of Abrasive Treatment and Preliminary Washing.

Experiments on various materials prepared in different ways gave results shown in Table XII.  The pre-treatment has a marked effect, but it appears to be due partly to removal or modification of oxides, and partly (in some cases) to organic matter left on the surface.

Series XIV.  Nature of Abrasive Treatment and Preliminary Washing.

TABLE XII.

| Abrasion. | Cleaning. | Probability, Per Cent. | Cond. Velocity (mg. per Drop Corroding). |
|---|---|---|---|
| *Carbonyl Iron in* 100 *per cent. Oxygen tested with* 0·0005 *M. Potassium Chloride.* | | | |
| FF149 Carborundum | Brushed | 32 | 0·17 |
| FF149 Carborundum | Boiling water | 62 | 0·24 |
| FF149 Carborundum | Cold water | 13 | — |
| FF149 Carborundum | Carbon tetrachloride | 34 | 0·21 |
| No. 3 paper | Brushed | 52 | 0·16 |
| No. 3 paper | Carbon tetrachloride | 82 | 0·22 |
| No. 3 paper | Boiling water, alcohol, acetone, petrol, carbon tetrachloride, toluene | 73 | 0·17 |
| No. 1F paper | Brushed | 61 | 0·11 |
| No. 1F paper | Carbon tetrachloride | 95 | 0·15 |
| *Steel* H-33 *in Purified Air tested with* 0·001 *M. Potassium Chloride.* | | | |
| No. 3 paper | Brushed | 22 | 0·06 |
| No. 1F paper | Brushed | 76 | 0·12 |
| No. 00 paper | Brushed | 79 | 0·08 |
| *Wrought Iron* 15 *in* 100 *per cent. Oxygen tested with Pure Water.* | | | |
| FF149 Carborundum | Brushed | 55 | — |
| No. 3 emery paper | Brushed | 29 | — |
| FF149 Carborundum | Cold water | 5 | — |
| Milled | Brushed | 94 | — |
| Milled | Rubbed with glue | 100 | (Liquid extended over waxed areas thus connecting drops.) |

## Series XV.    Character of Scratch-line.

Experiments by the scratch method with variable loads were carried out on steel B-32, using 0·14 *M*. sodium bicarbonate as the liquid and oxygen as the atmosphere. The results are shown in Table XIII. It is clear that increasing the weight on the needle increases the probability.

| Grams Weight on Needle. | Probability, Per Cent. |
|---|---|
| 100 | 19 |
| 200 | 38 |
| 400 | 44 |
| 800 | 52 |

## Series XVI.    Protective Effect of Neighbouring Scratch-lines.

As explained elsewhere,[21] corrosion occurring at one point should on theoretical grounds depress the probability of corrosion at neighbouring points below the *a priori* value, in cases where the anodic polarisation needed to maintain corrosion is less than that needed to initiate it ; electrochemical measurements have shown this condition to be fulfilled for iron.[22] Special causes for the relative immunity of the area around a corroding point may be the production of soluble alkali, *e.g.* sodium hydroxide, or a protective layer, *e.g.*, calcium carbonate, over the cathodic regions. The depression of probability by neighbouring corroding points has already been demonstrated quailtatively by the authors.[23] To obtain a *quantitative* measure of the depression, experiments were carried out on steel B-32, using oxygen and 0·14 *M*. sodium bicarbonate. Each cell contained two scratches made respectively two hours and about half a minute before the experiment. The fresh scratch almost invariably produced attack and this depressed the probability of corrosion at the older scratch, especially when the distance was small. The results are shown in Table XIV.

**Series XVI.    Protective Effect of Neighbouring Scratch-lines.**

TABLE XIV.

| Distance Between Adjacent Scratches. | Probability of Old Scratch Corroding. | Probability of New Scratch Corroding. |
|---|---|---|
| ∞ (one scratch per cell) | 69 per cent. | — |
| 4 mm. | 44  ,,    ,, | 94 per cent. |
| 2  ,, | 33  ,,    ,, | 96  ,,    ,, |
| 1  ,, | 19  ,,    ,, | 96  ,,    ,, |

## Discussion.

As explained elsewhere,[24] corrosion usually stifles itself at any point where it produces an insoluble product in physical contact with the metal, but continues if this insoluble substance is precipitated at a sensible distance. In attack by distilled water below an oxygen-rich atmosphere, the initial product, ferrous hydroxide, will be converted into the less soluble hydrated ferric oxide in physical contact with the metal, stifling the attack ; the surface will either remain unchanged,

[21] U. R. Evans, *Kohlschütter-Festschrift*, 1934 (*Kolloid Zeitschrift*, **68**, 135, 1934).
[22] S. C. Britton and U. R. Evans, *J. Chem. Soc.*, 1773, 1930.
[23] R. B. Mears and U. R. Evans, *Trans. Faraday Soc.*, **30**, 421, 1934.
[24] U. R. Evans, *Treizieme Congres de Chimie Industrielle*, 1933. The theory is essentially the same as that of the late J. F. G. Hicks, *J. Physic. Chem.*, **33**, 780, 1929.

or if the film of hydrated ferric oxide is thick enough, will show the weak interference tints noted in studies of drop-corrosion by Lewis.[25] If the supply of oxygen is insufficient, this secondary change will occur at a distance, producing loose rust and allowing continued etching of the metallic surface. This explains why the probability decreases with the oxygen content, and the conditional velocity rises.

Where potassium chloride solution is the corrosive liquid, the primary anodic product, ferrous chloride, is precipitated as hydrated ferric oxide by the cathodic product, potassium hydroxide, and oxygen ; but since the cathodic formation of potassium hydroxide is stimulated by oxygen (a cathodic depolariser), it is clear that here also a rapid supply of oxygen will favour the stifling of the reaction ; but supposing that the production of ferrous chloride be locally too rapid for precipitation *in situ*, oxygen will clearly increase the velocity.

The fact that liability to attack is often depressed by pre-exposure to oxygen points to an oxide film as the influence restraining the supply of ferrous compounds ; the more nearly perfect the primary oxide film, the smaller is the supply of oxygen needed to ensure that the secondary product is precipitated in such a manner as to stifle attack. (Much of the argument which follows, however, would apply equally to any " energy-barrier "—not necessarily a material screen—capable of preventing the passage of metallic ions from the lattice to the liquid, except at certain weak points in the screen).

The measurements of Bengough, Lee and Wormwell [26] on the corrosion of zinc at different depths indicate that, through *deep* columns of liquid, oxygen travels by *convection*, but that *diffusion* predominates in *shallow* layers (comparable to the thickness of drops). Maass and Liebreich [27] have indeed demonstrated convection currents in drops, the circulation being maintained apparently by evaporation ; these currents, however, should be absent in a saturated atmosphere—such as has been used in the present research. Convection currents due to falling corrosion products, as studied on vertical specimens,[28] might perhaps operate in freely corroding drops, but hardly under critical conditions. Probably, therefore, diffusion is the main form of transport, and the rate of supply of oxygen will be proportional to $C_1 - C_2$. where $C_1$ and $C_2$ are the oxygen concentrations at the liquid-gas and liquid-metal interfaces respectively. At the critical concentration, where oxygen just ceases to reach the metal sufficiently quickly to produce precipitation *in situ*, $C_2$ must be very small, and thus the rate of arrival and consequently the rate of consumption of oxygen is approximately proportional to $C_1$. Assuming Henry's law, it follows that the oxygen-pressure needed to prevent corrosion at a pore in the film is proportional to the maximum rate of production of ferrous compounds, and is thus a rational measure of the " size " of the pore.

If $Q_P$ be the "ideal density of distribution" of pores of sufficient size to produce corrosion at all oxygen pressures up to $P$ (the "ideal density " being defined by stating that the probability of attack on a

[25] K. G. Lewis, *unpublished work.*

[26] G. D. Bengough, A. R. Lee and F. Wormwell, *Proc. Roy. Soc.*, 131A, 500, 1931.

[27] E. Maass and E. Liebreich, *Korrosion und Metallschutz*, 6, 49, 103, 172 1930 ; U. R. Evans, *ibid.*, 6, 74, 173, 1930 ; U. R. Evans and C. W. Borgmann *Z. physik. Chem.*, 160A, 200, 1932.

[28] U. R. Evans and T. P. Hoar, *Proc. Roy. Soc.*, 137A, 355, 1932. U. R. Evans and R. B. Mears, *Proc. Roy. Soc.*, 146A, 160, 1934.

small area $da$ is $Q_p\,da$), then, *assuming mutual independence of events,* the *expected number* of breakdown points at this pressure in a drop of area $A$ would be $Q_P A$ and the probability of $n$ breakdowns would be given approximately [29] by the Poisson expression $\dfrac{(Q_P A)^n e^{-Q_P A}}{n\,!}$. Actually, since the appearance of one breakdown reduces the chance of others, the expected number will be less than $Q_P A$ and the Poisson expression will only be valid when $n = 0$. Considering this special case, the chance of obtaining *no* breakdowns in a drop becomes equal to $e^{-E}$, where $E$ is the number which would be expected assuming mutual independence of events. ($E$ is equal to $Q_P A$ for a "uniform drop," or to $\int Q_P da$, if account is taken of the alteration of $Q_P$ near the edges). Thus the chance of one or more breakdowns is

$$p_{>0} = 1 - e^{-E}.$$

This probability $(p_{>0})$ has been measured for different oxygen concentrations in Series III. From these values it is possible to calculate $E$. Fig. 6 shows the relation of $E$ to the oxygen pressure $P$ for three materials. Since the minimum pressure needed to smother corrosion at a pore is a measure of the size of the pore, the gradient $dE/dP$ should show the relative frequency of pores of different sizes; it is clear that
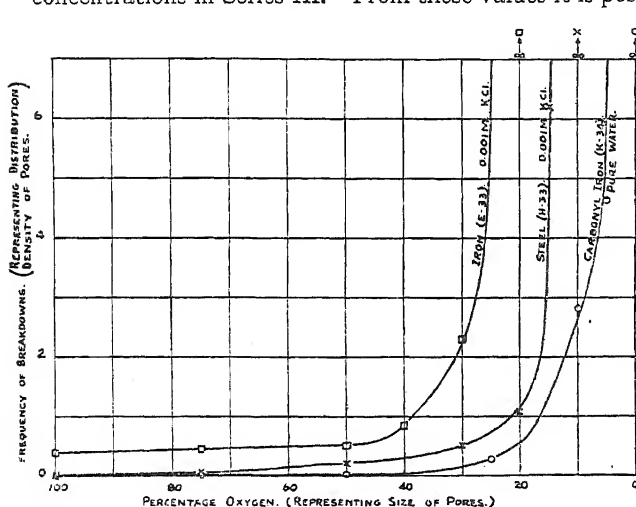


FIG. 6.

the pores become more frequent as the size under consideration becomes smaller. This conclusion is permissible whether the rate of production of ferrous salts at pores of different sizes (in the absence of oxygen on the spot), is proportional to the perimeter $(2\pi r)$ or to area $(\pi r^2)$ of the pores in question (or more generally to $k_1 r + k_2 r^2$).

We are led, therefore, to a conclusion very similar to that reached, by a totally different argument, from studies of the time-thickness curves of silver iodide films grown at different temperatures, concentra-

[29] Mr. H. E. Daniels and Mr. R. W. Morris of the Mathematical Department have very kindly investigated at some length the validity of Poisson's Theorem as applied to the present problem. Two alternative treatments (one of which is independent of Poisson's Theorem, but is possibly open to other objections) lead respectively to the values of $1 - e^{-E}$ and $1 - e^{-1.05E}$ for $p_{>0}$ in the case of 27 drops. The first treatment yields exactly the same curves as those shown in Fig. 6, whilst the other yields the same curves if the scale of $E$ is contracted by 5 per cent. All three treatments lead to the same final conclusions.

tions and using different solvents.[30]  Instead of a definite number of
" holes " in an otherwise perfect film, we have to picture a film-substance
which is specifically porous, the pores becoming increasingly rare as the
pore-size under consideration becomes larger.  A film becomes pro-
tective only under such conditions which enable even the largest pore
present to block itself with corrosion products, thus stifling attack before
it becomes visible.  With films containing only very small pores (*e.g.*,
the films on stainless steel or aluminium), this can happen under ordinary
conditions, whilst with films containing larger pores (*e.g.* the film on
ordinary iron), it will occur only under exceptional conditions.  There
has been much discussion as to whether it is the primary (air-formed)
film (usually oxide), or the secondary film of corrosion-products (often
hydroxide) which protects the metal.  It appears probable that in general
*both* contribute to the protection, but that the nature of the primary
skin decides whether the secondary product can be formed in physical
contact with the metal or not.  The smaller the pores in the primary
film, the more probable it is that they will be self-stifling ; the slighter
the damage to the primary film (produced by scratching, etc.), the
more probable it is that the damage will heal.

Certain so-called inhibitors like potassium hydroxide and potassium
carbonate tend to depress the anodic reaction, but stimulate the cathodic
reaction by leaving a larger surface available as cathode.  On metals
like iron where (in the absence of the inhibitor) the cathodic change
mainly determines the velocity, such additions may actually increase
the conditional velocity ; but since an anodic change is an essential
part of the corrosion-process, sufficient additions must depress the prob-
ability.  This is found to occur not only with the alkaline inhibitors
mentioned, but also with oxygen.  The action of oxygen is, however,
not quite analogous, since it stimulates the cathodic reaction largely
through depolarisation.

## Summary.

(1) Measurements have been made of the influence of sixteen external
variables on (*a*) the Probability and (*b*) the Conditional Velocity of cor-
rosion by drops.  Oxygen-concentration *depresses* the probability but
*increases* the conditional velocity ; the same is true of certain recognised
inhibitors (*e.g.* potassium carbonate).  Pre-exposure to oxygen depresses
the probability of attack by certain liquids (0·07 $M$. sodium bicarbonate),
but not by others.  A rise in the *temperature of pre-exposure* tends somewhat
to depress the probability, whereas a rise in the *temperature of experiment*
greatly increases the probability, as does also the presence of sulphur dioxide
in the gas phase ; carbon dioxide does not appreciably increase the prob-
ability, but stimulates the conditional velocity.  With increase of potas-
sium chloride, the probability rises, while the conditional velocity first
rises and then falls again.  The presence of neighbouring corroding points
depresses the probability (" mutual protective effect ").  A comparison
has also been made of different drop sizes, different irons and steels, different
varieties of distilled water, different anions, different inhibitors, different
$p_H$ values, different abrasive treatments, different cleaning treatments, and
different forms of scratch lines.

(2) Assuming that inhibition occurs only when the corrosion-product
formed at a pore in an oxide film is precipitated in physical contact with
the metal, thus stifling attack, it is shown that the oxygen-concentration
needed to prevent corrosion in a drop is a suitable measure of the size of

[30] U. R. Evans and L. C. Bannister, *Proc. Roy. Soc.*, 125A, 370, 1929.

the biggest pore. From the data connecting probability and oxygen-concentration, it is shown that the pores grow continuously more frequent as the "size" under consideration is reduced, thus indicating that the film-substance possesses an essentially porous character—a conclusion analogous to that reached, by a different argument, after experiments on the growth of silver iodide films.

# VISCOSITY, VAPOUR PRESSURE AND LATENT HEAT.

By J. Newton Friend.

The viscosity of a liquid depends to an unusual degree upon its molecular structure, any slight change in which may exert a disproportionately large effect upon the viscosity. Although at present the results may be difficult to interpret there can be little doubt that eventually viscosity data will prove as valuable to the physical chemist as surface tension data are proving now that Sugden has introduced the parachor. There is this important difference, moreover, that whilst surface tension is essentially a surface phenomenon, viscosity is concerned with the internal properties of a

TABLE I.

| Absolute Temperature. | Octane. | Methyl Butyrate. | Toluene. | Chlor-benzene. |
|---|---|---|---|---|
| 303° | 0·369 | 0·498 | 0·473 | 0·502 |
| 313° | 0·362 | 0·495 | 0·468 | 0·491 |
| 323° | 0·361 | 0·495 | 0·466 | 0·491 |
| 333° | 0·360 | 0·495 | 0·466 | 0·488 |
| 343° | 0·361 | 0·498 | 0·461 | 0·489 |
| 353° | 0·364 | 0·498 | 0·464 | 0·492 |
| 363° | 0·363 | 0·496 | 0·463 | 0·489 |
| 373° | 0·366 | 0·498 | 0·466 | 0·492 |
| 383° | 0·365 | — | 0·467 | 0·490 |
| 393° | 0·362 | — | — | 0·491 |
| Boiling Pt. (abs.) A | 399° 247·4 | 375° 237 | 384° 236·4 | 405° 247·8 |

liquid and may therefore be expected to respond with great sensitiveness to changes in molecular configuration.

As our knowledge of the structure of liquids and of the forces involved in cohesion, etc., is as yet slight it is inevitable that some of the simpler relationships between liquid properties shall be empirical. This paper is based on the empirical observation that, over a considerable range of

temperature in the neighbourhood of the boiling-point of pure, un-associated liquids, the product of the viscosity, $\eta$, into the square root of the vapour pressure, $p$, rises linearly with the temperature. This observation leads to several interesting results.

We may write

$$\frac{\eta p^{\frac{1}{2}}}{T_1 - A} = B \qquad . \qquad . \qquad . \qquad . \qquad (i)$$

where $T_1$ is the absolute temperature, whilst $A$ and $B$ are constants the meanings of which are discussed later. In this paper $\eta$ is expressed in millipoises. Associated liquids do not, in general, obey this rule. In Table I. are given the values of $A$ and $B$ for several typical liquids. It will be noted that $B$ is constant over most of the temperature ranges for which the viscosity data are available.

For any two temperatures $T_1$ and $T_2$ we obtain, on logarising equation (1),

$$\log \frac{p_2}{p_1} = 2 \log \frac{\eta_1}{\eta_2} \cdot \frac{T_2 - A}{T_1 - A} \qquad . \qquad . \qquad . \qquad (ii)$$

In the immediate vicinity of the boiling-point, when $T_2 - T_1$ is small, the ratio $\eta_1/\eta_2$ does not differ appreciably from $(T_2 - A)/(T_1 - A)$. Equation (ii) may therefore be written as

$$\log \frac{p_2}{p_1} = 4 \log \frac{\eta_1}{\eta_2} \qquad . \qquad . \qquad . \qquad . \qquad (iii)$$

$$= 4 \log \frac{T_2 - A}{T_1 - A}. \qquad . \qquad . \qquad . \qquad (iv)$$

The examples given in Table II. illustrate equation (iii); the viscosity ratios are calculated from the data given by Thorpe and Rodgers[1] and the vapour pressure ratios from the data in the Int. Crit. Tables. The temperature intervals chosen are those nearest the boiling-points. Despite the largeness of the interval ($10°$ C.) the agreement is good.

TABLE II.

| | Temp. Range, °C. | Boiling Point, °C. | $\log_{10} \frac{p_2}{p_1}$ | $4 \log_{10} \frac{\eta_1}{\eta_2}$ |
|---|---|---|---|---|
| Hexane | 50–60 | 69 | 0·14993 | 0·15052 |
| Bromine | 40–50 | 58·8 | 0·15800 | 0·15792 |
| Chloroform | 50–60 | 61 | 0·14800 | 0·14968 |
| Methyl propionate | 60–70 | 79·7 | 0·15866 | 0·15840 |
| Toluene | 100–110 | 111 | 0·12905 | 0·13052 |

To find an expression connecting latent heat, $l$, with viscosity it is only necessary to combine equation (iii) with the Clausius-Clapeyron equation. We then obtain

$$l = 2·3 \times 4 \times \frac{R}{M} \cdot \frac{T_1 T_2}{T_2 - T_1} \cdot \log_{10} \frac{\eta_1}{\eta_2} \qquad . \qquad . \qquad (v)$$

Where $M$ is the molecular weight, $R$ the gas constant ($1·985$), $l$ being expressed in gram-calories.

[1] *Phil. Trans.*, **185**, 397, 1895; **189**, 71, 1897.

The examples in Table III. illustrate this. The substances selected are typical; they show considerable variation in their latent heats and chemical natures. In the fourth column are given the latent heats as calculated with the aid of the Clausius-Clapeyron equation from the vapour pressures over the same temperature intervals; in the fifth column are given the latent heats, at the temperatures given in parentheses, as obtained by direct experiment.[2]

TABLE III.

| Substance. | Temp. Range, °C. | $l$ (Equation V.). | $l$ (from V.P.). | $l$ (Observed). | $\frac{A}{T}$. |
|---|---|---|---|---|---|
| Bromine | 40-50 | 45·7 | 45·7 | 43·7 (63°) | 0·625 |
| Chloroform | 50-55 | 61·6 | 61·0 | 59·0 (61·5°) | 0·627 |
| Ethyl bromide | 20-30 | 60·5 | 61·3 | 59·9 (38·4°) | 0·639 |
| Pentane | 20-30 | 88·2 | 98·3 | 84·3 (40°) | 0·620 |
| Isopentane | 10-20 | 87·1 | 87·3 | 88·7 (13°) | 0·608 |
| Hexane | 50-60 | 85·9 | 80·6 | 79·4 (68°) | 0·622 |
| Methyl acetate | 40-50 | 101·9 | 104·2 | 98·1 (56·3°) | 0·655 |
| Ethyl acetate. | 60-70 | 96·4 | 93·1 | 85·8 (80°) | 0·639 |
| Toluene. | 100-110 | 92·6 | 91·5 | 86·6 (109·6°) | 0·616 |
| m-Xylene | 120-130 | 83·5 | 85·3 | 81·2 (138·5°) | 0·634 |

The values of $l$ calculated from the viscosity are in general in quite as good agreement with the experimental values as those calculated from the vapour pressures. The agreement is as close as can be expected from existing viscosity data. As is evident from equation (iii) any small error in $\eta$ must have a relatively large effect upon the value of $l$. Conversely if $l$ and $\eta$ are known with accuracy, equation (v) should be a sensitive indicator of association.

It may be noted in passing that the good agreement for bromine, calculated on the assumption that the liquid is diatomic, affords independent support to that view.

Equation (v) may be written in the form

$$\log_{10} \eta = \frac{a}{T_1} + b. \quad . \quad . \quad . \quad . \quad (\text{vi})$$

Where $a$ and $b$ are constants. This is the equation obtained by Sheppard and independently by Andrade (1930). The constant $a = Ml/2 \cdot 3 \times 4 \times R$ and is thus one quarter of the value of the equivalent constant in the corresponding vapour pressure equation in the neighbourhood of the boiling-point.

Equation (v) may be written

$$l = 2 \cdot 3 \times 4 \times \frac{R}{M} \cdot \frac{T_1 T_2}{T_2 - T_1} \cdot \log_{10} \frac{T_2 - A}{T_1 - A} \quad . \quad . \quad (\text{vii})$$

and will give similar results if $A$ is known. $A$ approximates to $0 \cdot 625T$, where $T$ is the boiling-point (see Table III.). Hence if $A$ is not known for a particular substance this approximate value may be taken. For

[2] *I.C.T.*, vol. v., p. 135 *seq.*

unit temperature interval at the boiling-point equation (vii) then sim-
plifies to

$$l = 2 \cdot 3 \times 4 \times \frac{R}{M} \cdot T(T - 1) \log_{10} \frac{T}{T - 2 \cdot 67} \cdot \qquad . \quad \text{(viii)}$$

Between the limits $T = 100$ and $1000°$ abs. the value of the expression
$(T - 1) \log_{10} \dfrac{T}{T - 2 \cdot 67}$ ranges from $1 \cdot 162$ to $1 \cdot 159$ and may be regarded
as constant. Inserting the mean value $1 \cdot 16$ into the equation, and re-
placing $R$ by $1 \cdot 985$ we have, on rearranging the terms,

$$\frac{Ml}{T} = \text{constant} = 21 \cdot 2.$$

This is Trouton's Rule.
Writing $A = 0 \cdot 625T$ it becomes evident from equation (1) that $BT \propto$
the viscosity at the boiling-point. If $p = 760$ mm., $BT = 73 \cdot 5\eta$ at
the boiling-point.

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# ON THE VARIATION OF THE DIELECTRIC CONSTANT OF IONIC CRYSTALS WITH TEMPERATURE.

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South Kensington.*

The variation of the dielectric constant of crystals has been calculated
by Bretscher [1] and compared with experimental results.
   The method adopted by Bretscher was as follows : The dielectric
constant $\epsilon$ is obtained from the well-known formula

$$\epsilon = \epsilon_0 + \frac{K\rho}{\omega_0^2} \cdot \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

in the case where we have only one *Eigenfrequenz.*
   The variation of $\epsilon$ with temperature is hence due to the variation
of $\rho$ and of $\omega_0$ with temperature. The method adopted by Bretscher
is to separate these two effects, the first being calculated from the
Lorenz-Lorenz formula

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{\rho} = \text{const.}$$

and the second effect from the Grüneisen [2] formula

$$\frac{1}{\omega_0} \frac{\partial \omega_0}{\partial t} = - \frac{n + 2}{6} \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p,$$

where $n$ is the exponent in the repulsive forces between particles.

[1] E. Bretscher, *Trans. Faraday Soc.,* **30**, 9, 684, 1934.
[2] E. Grüneisen, *Geiger-Scheel Handbuch der Physik X.*

The results obtained in the case of NaCl and $CaF_2$, do not agree at all well with experiment; this is attributed by Bretscher to three possible causes :

(i) the possible existence of other *Eigenfrequenzen* in the case of NaCl as indicated by the work of Czerny;[3]

(ii) the possibility that the law of repulsion was not sufficiently correct;

(iii) that the treatment was "monochromatic" *i.e.* that the use of the Grüneisen formula might not be justified.

With regard to (i), it has been shown [4] that the subsidiary maxima found by Czerny and his collaborators are not to be considered as real *Eigenfrequenzen*. The damping coefficient for very long waves will show no abnormal behaviour and hence equation (1) holds good.

The second point raised (ii) is probably not of importance because this law of force has been used very successfully in calculating the position of the *Eigenfrequenzen* of the alkali halides.

The real reason for the discrepancy lies in (iii) : the theory of Grüneisen should be replaced by the more exact formulæ based on the lattice theory of Born.[5]  This gives the value of $\omega_0$ in the form

$$\omega_0{}^2 = \sqrt{\left(\frac{1}{m_1} + \frac{1}{m_2}\right)(\Delta \,.\, D + uD' \,.\, \Delta)} \qquad . \qquad . \quad (2)$$

where $m_1$ and $m_2$ are the masses of the ions,

$$\Delta \,.\, D + uD' \,.\, \Delta = \frac{S_0(1)}{3} \frac{e^2}{r_0{}^3}(f_3(n) - uf_3'(n)),$$

$$S_0(1) = 1\cdot747 ;$$

$f_3(n)$ and $f_3'(n)$ are lattice sums, tabulated in Born and Brody's [6] paper;

$u = \alpha T$ where $\alpha$ is the coefficient of linear expansion and $T$ is the absolute temperature;

$e$ and $r_0$ are the charge and lattice constant, respectively.

Using the known values of $\alpha$ and $n$ we can calculate the dependence of the dielectric constant on the temperature from the formula :

$$\frac{1}{\epsilon}\frac{d\epsilon}{dT} = \frac{\epsilon - \epsilon_0}{\epsilon} \cdot \frac{\alpha f_3'(n)}{f_3(n)}.$$

The value for NaCl is $3\cdot27 \times 10^{-2}$ as compared with the experimental value of $3\cdot80 \times 10^{-2}$. This agreement as compared with Bretscher's value of $2\cdot12 \times 10^{-2}$, shows that the lattice theory does give reasonably good values.

## Summary.

The temperature coefficient of the dielectric constant has been calculated from Born's lattice theory ; a comparison with experiment is given in the case of NaCl.

[3] M. Czerny, *Z. Physik*, **65**, 600, 1930.
[4] M. Born and M. Blackman, *Z. Physik*, 82, 555, 1933.
[5] M. Born, *Atomtheorie des festen Zustandes*.
[6] M. Born and E. Brody, *Z. Physik*, 11, 327, 1922.

# ON THE KRYPTON CONTENT OF ATMOSPHERIC AIR.

By Dr. I. Brody and Dr. F. Körösy.

The quantitative determination of the rare gases krypton and xenon in the atmosphere is difficult to carry out and its literature is therefore scarce. Sir W. Ramsay, discoverer of the rare gases, published an estimate of their concentration[1] which subsequently proved to be remarkably correct. He amended[2] later the value of $1 \times 10^{-6}$ first given to $5 \times 10^{-8}$ and made yet another correction[3] which gave rise to widespread misunderstanding throughout the whole literature.[4]

Ramsay's method was fractional distillation. It is evident, that the losses during this process can scarcely be estimated, so that the whole result is built up upon this dubious estimation. This is the reason of the great divergence between the results of 1900 and 1903, and it is noteworthy that the first estimation gave the right order of magnitude.

An essentially different method was presented by Ch. Moureu and A. Lepape. They were interested in the ratio of rare gases in thermal springs and worked out a method to compare the ratio of Kr : Ar in a given gas to that in the air.[5] They first removed the non-inert gases by chemical processes and went on to concentrate the krypton and xenon in a carefully normalised adsorption process by $-23°$ C. on cocoanut charcoal. The adsorbed fraction was liberated and passed into a " Plücker " discharge tube, and subjected to the discharge of a Ruhmkorff inductor whereupon the intensity of the krypton line 5871 Å. relative to the argon lines 5861 Å., 5882 Å., 5888 Å. was determined visually. Unfortunately no details of this obviously difficult visual method were published, so that it is impossible to judge the basis upon which the authors estimated the error to be about 10 per cent. So far all the measurements referred only to the krypton : argon ratio in the air as a standard ; it was not until nine years later that Moureu and Lepape[6] determined this ratio itself. They made " standard solutions " of pure krypton in pure argon using a dilution containing 2·17 per cent. krypton as an intermediate. They determined now, not the intensity-ratio of spectral lines, but the gas pressure at which the intensities of the krypton line and the argon line chosen were equal. It was proved that between krypton concentrations of $0·46 \times 10^{-3}$ and $4·3 \times 10^{-3}$ and between pressures of 12·5 and 1·4 mm. the product of pressure by concentration remained fairly constant and the method was reliable. Gases with a higher krypton content have to be diluted,

[1] W. Ramsay and M. W. Travers, *Proc. Roy. Soc.*, **67**, 329, 1900.

[2] *Ibid.*, **71**, 421, 1903 ; *Z. physik. Chem.*, **44**, 74, 1903.

[3] *Proc. Roy. Soc.*, **80**, 529, 1908.

[4] E. Rabinowitsch, *Z. angew. Chem.*, **39**, 737, 1926.

[5] *Compt. rend.*, **152**, 740, 847, 1043, 1911.  *J. chim. physique*, **11**, 63-152, 1913, especially pp. 105-114.

[6] *Compt. rend.*, **174**, 908, 1922.

those with less have to be concentrated by absorption in the above-mentioned manner. The method was then applied to the rare gases of the air.[7] They were adsorbed on charcoal at $-79°$ C., nine-tenths were pumped off and the remainder, containing *all* (?) the krypton was examined spectro-photometrically. The mean value of 12 measurements gave $1·05 \times 10^{-4}$ with an error of 10 per cent. A brief control of the results with synthetic mixtures of the same krypton content seemed to reveal an error : the authors found systematically some 13 per cent. less krypton than calculated, presumably owing to incomplete adsorption. Unfortunately the experiments of Moureu and Lepape had to be broken off at this stage of the work. Correcting their above values by 13 per cent. and allowing 10 per cent. for the error, their result is $1·0$ to $1·31 \times 10^{-4}$ krypton : argon (parts by volume). It is worthy of mention that two years later G. Claude [8] succeeded in isolating effectively $0·6 \times 10^{-6}$ parts of krypton from air, thereby giving an absolute lower limit for further determinations.

Summarising, the result of Moureu and Lepape seems to be trustworthy but it was of interest to control it by an *objective* method which was independent from all fractional distillation and adsorption.

## Experimental.

### 1. The Method.

We desired to exclude all doubts arising from fractional distillation or adsorption and therefore rejected both operations. By purely chemical procedure we removed everything from the air except the rare gases. This residue was not fractionated further. We used it to get a spectrogram of its emission in an electric discharge and determined the relative intensity of the spectrum lines of krypton in relation to some of the weaker argon lines. On the other hand we prepared a series of argon—krypton mixtures with varying known krypton contents, determined the relative intensity of the same lines in these also, and calculated the krypton content of " air argon " by interpolation.

Thus our method is similar to that used by Moureu and Lepape, differing only in the following points : (1) we did not make use of fractional adsorption but worked with the original, dilute krypton-argon mixture ; (2) we substituted the objective spectrographic method in place of the subjective spectroscopic one of the French authors ; (3) we did not regulate the pressure of the gas so as to attain equal luminosity of the argon and krypton lines, but compared quantitatively the said intensities after having determined the characteristic sensibility curve of the photographic plates.

### 2. Purification and Mixing of the Gases.

The rare gases of the air were obtained by means of an electric furnace containing calcium metal at $600-700°$ C. The calcium was activated by a small quantity of sodium. The velocity of reaction was very great : so long as the calcium was fresh, it amounted to about $0·3$ l. air per minute. 50 l. air was consumed in this manner. The remainder ($0·5$ l.) of rare gases was sealed off in three separate containers, each of which was equipped with a small nickel-molybdenum furnace. The volume of this furnace was about 4 c.cm. ; it was filled with barium metal powder and could be heated with 40W. by means of protected tungsten filaments. The vaporised barium removed all impurities which may have escaped the action of the calcium furnace.

[7] *Compt. rend.*, **183**, 171, 1926.          [8] *Ibid.*, **187**, 581, 1928.

The argon was furnished in steel flasks from an air liquefying plant and was treated with active charcoal, at $-80°$ C. and 15 mm. pressure, to remove the last traces of krypton. It was then subjected to a discharge between calcium electrodes, the calcium of which vaporised and removed the nitrogen which amounted to about 3 per cent. of the argon. Finally, the pure argon was filled into a container with a barium furnace as described above, and was ultimately purified with barium vapour. The blue krypton line 4319 Å could not be detected in this argon, but the yellow line at 5871 Å never quite disappears [9] because of the coincidence with an argon line. The latter has the wave length $5870 \cdot 26$ whereas the former lies at $5870 \cdot 92$ Å.

The krypton (from the Linde Gesellschaft) was purified in the manner described above with barium vapour. Its molar weight was found to be $84 \cdot 2$ to $84 \cdot 3$ instead of $83 \cdot 6$. Its spectrum betrayed the presence of some xenon and argon ; the difference between its molar weight and that of pure krypton may be due to its xenon content.[10]

The dilute krypton-argon mixtures could not be prepared in a single operation, because the necessary partial pressure of krypton was extremely low. Indeed it was so low that, even when we diluted the gas in two steps, great care was needed to exclude errors arising from adsorption.

The mixing was performed in the glass bulb *4* (Fig. 2) which had a volume of about 750 cm.$^3$ and a surface of about 500 cm.$^2$ The tube volumes between the stopcocks *a*, *c*, *e* and *4* were negligibly small, so that all the gas entered *4* and could be thoroughly mixed there by heating the tungsten coil with about 20 watts.

Experiments showed that the bulb wall adsorbed more than $0 \cdot 1$ mm. krypton in saturation ; this is in fair agreement with a calculation on basis of monomolecular adsorption which yields about $0 \cdot 05$ mm. The difference is probably due to the difference between macroscopic and adsorptive surface. If we had to mix a diluted (1 per cent.) krypton-argon mixture with pure argon, so as to obtain a mixture with $5 \times 10^{-5}$ krypton and wanted to spare the pure argon, we chose a total end pressure of about 20 mm. Thus, only $0 \cdot 1$ mm. of the dilute mixture was needed : a quantity commensurable with that adsorbed on the bulb surface. If we had allowed the dilute krypton to enter first into the mixing bulb, an error of about 50 per cent. would have been caused, because about one-half of it would have been adsorbed and it was impossible to say how much of this would evolve during the period when the mixing coil was heated. We therefore always began by blocking the bulb surface with pure argon, until the pressure on the McLeod gauge was read to about $0 \cdot 2$ mm. The adsorbed argon (say $0 \cdot 1$ mm.) could reasonably be neglected in relation to the whole argon pressure of 10-20 mm. The dilute krypton was only allowed to enter after this small quantity of argon was present. The additive pressure ($0 \cdot 1$ to $1 \cdot 0$ mm.) was read on the McLeod ; finally we let in the main part of argon and mixed thoroughly. In this manner we first prepared our dilute " stock " solution containing $0 \cdot 89 \pm 0 \cdot 02$ per cent. krypton in pure argon and used this stock solution in preparing the definite mixtures ; always on the principle of blocking the bulb surface.

## 3. The Discharge Tubes.

Geisler tubes of the ordinary type gave far too small light intensities for our purpose : the krypton lines appeared only after exposures of 8-24 hours. In addition to the obvious inconvenience resulting from long exposures, we found that an appreciable part of the krypton was apt to vanish in the tubes, as a result of the clean up effect of sputtered electrodes.

[9] Ch. Moureu and A. Lepape, *J. chim. physique*, 11, 108, 1913.
[10] *Added in Proof.*—In a recent communication F. J. Metzger (*J. ind. eng. chem.*, 27, 115, 1935) states that he also failed to fractionate pure krypton below a density which indicated the presence of $1 \cdot 5$ per cent. xenon. This amount of xenon would explain the difference in molar weight mentioned above. A revision of the molar weight of krypton appears to be necessary.

We had to construct a special type of spectral tube, (Fig. 1) with the following features :   The tube had an indirectly heated barium oxide cathode (heating: 4V., 2·3 Amp.) (*1*) so that no high voltage was necessary and sputtering could be avoided.   The molybdenum ring *2* served only as an auxiliary anode during the cathode activation, whereas the main anode *3* was made of 0·3 mm. molybdenum sheet and was soldered with the help of a small strip of nickel.   The vertical incisions served to adapt its high frequency resistance to that of our induction coil in which the anode could be baked out.   The glass bulb *4* is a reserve volume of 100-200 c.c. to compensate temporarily the loss of gas though an eventual clean up.

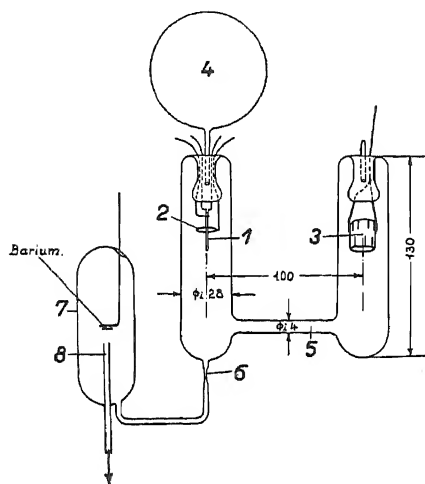The narrow tube (diam. 4 mm.) *5* was to be our source of light, " end on " before the spectrograph.   It had to support a charge of 2A. and 30V. (the total voltage between *1* and *3* was about 50V.) and proved to be the most delicate part of the apparatus. In spite of the fact that the tube was immersed in water, the slightest glass defect caused it to burst, especially when it was used for a second time.   Between *1* and *2* the discharge always began spontaneously but between *1* and *3* it was necessary to start it with a high frequency (Tesla) apparatus.   The tube was sealed at *6*, so that the barium " getter " in tube *7* did not remain in contact with the gas mixture.   The barium " getter " served for the ultimate purification of our gases, which entered through *8* and flowed directly against the barium



FIG. 1.

metal pellet.   This pellet was placed in a circular holder of nickel sheet and could be heated above the sublimation temperature of barium with an induction furnace.   In this manner the gas had to make its way in counter-current to barium vapour into the discharge tube, and was practically cleaned of all (even spectroscopic), traces of impurities, that is, of everything except the rare gases.   The exposure time with this type of discharge tube could be reduced to 1·5-3 hours and the results were quite satisfactory.

## 4. Preparation of the Discharge Tubes.

It was essential to clean the discharge tubes from all adsorbed impurities, before filling and sealing.   The three tubes *8*, on Fig. 2, and the little tube ncluding the barium pellet *7* (see also Fig. 1) were baked out first, without cooling any of the traps *6*, *9* and *10*, to a pressure below $10^{-3}$ mm.   Then the barium pellet and the three anodes were made red hot with an induction furnace and the cathodes were heated.   After 3-5 minutes the main portion of $CO_2$ evolved from the cathodes was pumped off and the circuit between the auxiliary anodes and cathodes could be closed.   The heating of the anodes was continued, until the discharge showed no $CO_2$ spectrum and trap *10* was then cooled with liquid air.   To remove the $CO_2$ blocking the glass walls, the tubes were again heated for about 45 minutes to 450° C., this time with a simultaneous cooling of the traps *6* and *9*, with $CO_2$-acetone. These traps served to freeze out all mercury-vapour, which was driven out by heating from *7*, *8* and, on the other hand, they prevented mercury

vapour from getting into *7, 8* from the McLeods *1, 11*. The baking was continued until the pressure sank below 10$^{-4}$ mm. in spite of the fact, that *4* was heated. After the above-mentioned vacuum was attained the discharge between cathodes and auxiliary anodes was switched on once more, an extra resistance being connected in series with each tube. The anodes were finally heated to red heat with the induction coil : some traces of mercury were still evolved as shown by the discharge. The discharge shortly ceased ; the tubes were clean.

The real anodes were then switched on instead of the molybdenum rings (120 V. with series resistances of about 50-100 Ohm) and gas could be admitted from *5*, or from *4*, according to whether atmospheric rare gas, or an artificial mixture was used. The mixing in *4* was described above. In spite of the baking out, the tubes *8*, especially the " capillaries " still contain contaminations. These can be removed by washing them with gas under discharge. A discharge of 1 Amp. could just be permitted and it cleansed the glass tubing from all traces of gas that could be evolved during a discharge, even without water-cooling. The tubes were filled three times with the gas and latter was pumped off, during discharge, from 2 mm. pressure to 10$^{-3}$ mm. Then *h* was closed, *7* heated so as to form barium vapour and the final gas filling was let in. A discharge was main-
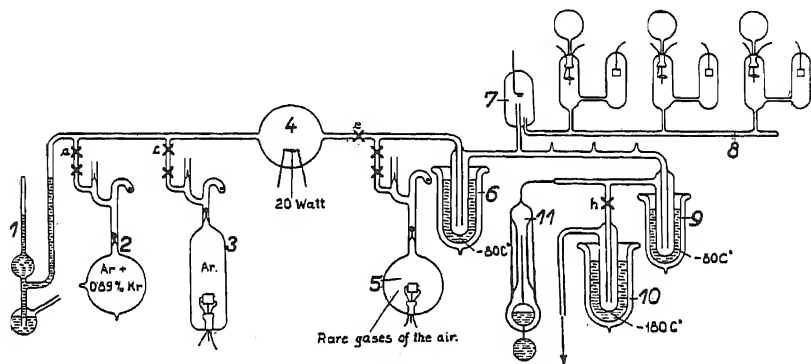


Fig. 2.

tained in the tubes for 10 minutes at 1 to 2 mm. pressure to saturate the glass walls with gas and postpone an eventual clean up ; then whilst the tubes cooled down the gas was pumped off till a pressure of 0·28 mm. was reached. The cold tubes were then sealed off. The pressure of 0·28 mm. is a compromise : the relative intensity of the krypton line would be greater at smaller pressures but the danger of the gas cleaning up limits any further attempt in this direction. The precision of mixing amounted to about 5-6 per cent. in the volume concentration of krypton.

## 5. The Optical Arrangement.

Owing to the facts, that the yellow krypton line 5871 Å. lies near to the argon line 5861 and the helium line 5875 and, moreover, that its intensity is extremely faint in the dilutions we have used, it was necessary to use instruments which had large relative aperture in addition to a dispersive power of at least 30 Å./mm. We made about half of the spectograms with a Schmidt and Haentsch spectroscope using its ocular lens to project an eightfold enlargement of the spectrum on the photographic plate. Thus we achieved a dispersion of about 12 Å./mm. in the region of the D lines. The second instrument (in the possession of the physical institute of the Technical University in Budapest) was kindly placed at our disposal by Prof. Dr. B. Pogány ; it is a Zeiss spectrograph with glass optical system

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and a dispersion of 28Å./mm. in the yellow and 8·7 Å./mm in the blue part of the spectrum. The results with both instruments correspond fairly well. It was impossible to make good spectra of the blue region with our spectrograph, because internal reflections caused yellow and green light to enter ; similar reflections could be observed, however, in the Zeiss instrument also. At normal exposures they may be negligible but they nearly ruined the spectra at the long exposures which were necessary to give the krypton line the desired blackening. Every spectrum line had a " ghost " on one side, a little below the normal line, so that only the top part of the normal lines could be safely used for measurements. The opening of the slit varied from 0·005 to 0·020 mm. on our own and from 0·05 to 0·07 mm. on the Zeiss spectrograph, being naturally constant during one series of spectra.

We had to determine the relation between the intensity of light and the blackening of the plate caused thereby for each plate and wave-length separately. We therefore photographed the customary " intensity marks " upon every plate using a series of grey glass (Schott a. Genossen Jena, " Grauglas N.G.5," 0·7 mm. thick) and increased their number after each mark, when working on our own spectrograph. A layer of this glass absorbed 40 per cent. of the light incident upon it. The spectrograms on the Zeiss instrument were kindly made for us by Dr. R. Schmied and Ing. Fränkel of the Physical Institute. The institute possesses the so-called " Hansen Stufenblende " which renders it possible to make 10 intensity marks at the same time, the relation of intensity between neighbouring marks being 1 : 1·67. It works absolutely achromatically.

We used " Agfa superpan " and " Ilford hypersensitive panchromatic " plates. The density of the spectra was registered with the " Zeiss Registrier-Mikrophotometer " of the said physical institut and partly with a similar instrument in the Zeiss-Werke, in Jena. The photometric plate of a spectrum 9 cm. long had the length of 18 cm. ; the distance between the darkest and lightest portions was about 70 mm. in the photometric curve.

## Evaluation of the Spectrograms ; Results.

Each photographic plate carries a series of spectra, including at least one spectrum of the atmospheric rare gases and an intensity scale (see Hansen-Blende and grey glass filters). Every spectrum was registered on the microphotometer and the intensity marks were registered also for a series of wave-lengths. From these latter, curves were constructed to show the relation between light intensity and photometric density of the plate. It was expedient to draw the light intensity in logarithmic scale. The intensity of a spectral line was determined, as usual, by subtracting from the light intensity, corresponding to the peak of the photometric curve, that intensity which would have replaced it, if the line were not there. The determination of this intensity, involves a somewhat dubious extrapolation : the photometric curve must be extrapolated graphically as a continuation of the two neighbouring lines (which are responsible for the residual blackening at this point) below the peak of the spectrum line in question. This value must now be expressed in terms of light intensity with the aid of the curve derived from the intensity marks. The extrapolation gives rise to an error which may be estimated on the curve and will be termed in the following as light error. *E.g.* the peak of the krypton line 5871 Å. was found to be at 46·4 mm. corresponding to 21·2 units of light, whereas the bottom of the curve was judged to lie between 56·8 and 58·0 mm. that is between 13·6 and 14·4 light units. Thus we determined that the line intensity lies between 6·8 and 7·6 light

units. An analogous process shows the intensity of the argon line 6279 Å. to lie between 10·4 and 10·7 units. The extreme limits of the relative intensity of krypton 5871/argon 6279 lines are thus given as 6·8/10·7 to 7·6/10·4, that is between 0·63 and 0·73.

These relative intensities of a krypton to an argon line are brought together in Fig. 3 (krypton 5871 Å. : argon 5784 Å.), and they are used to construct a straight line which represents the relative light intensity as a function of the krypton concentration. It is evident that any defect on the photographic plate completely alters the photometric result, so that the lack of precision in a single determination has to be corrected by determining a large number of individual points on the graph. We may mention that Fig. 3 contains *all* our determinations relative to the said pair of lines, without any correction. The points are represented
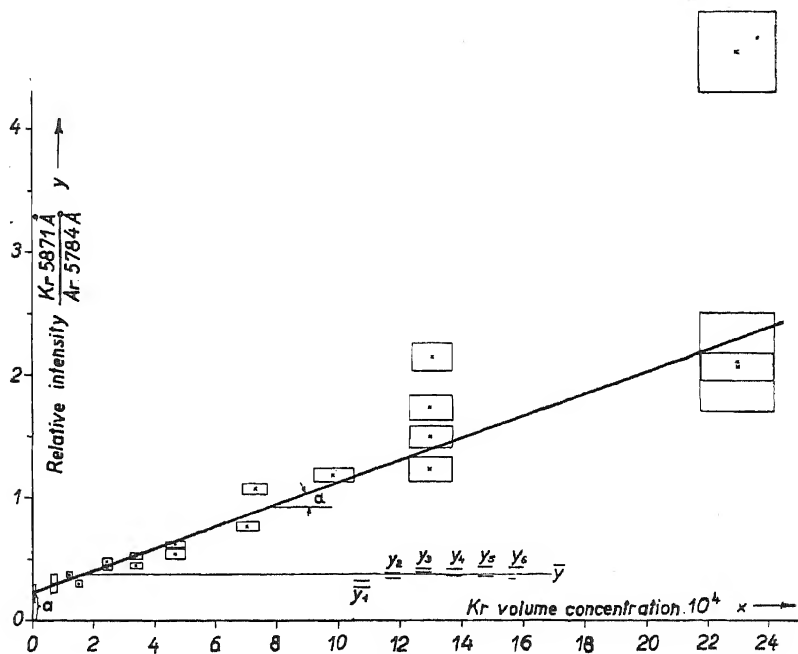


FIG. 3.

by rectangular oblongs : their height is equal to the " light error " and their breadth to the possible maximal error in the concentration of the respective mixtures. Thus the smallest area means the greatest reliability of a point and vice versa. The slope and the zero point ordinate of the line of Fig. 3 is a result of calculation on the principle of least squares. The individual weight of each point was put inversely proportional to its light and concentration errors. The existence of a positive zero point ordinate is due to the fact that the yellow krypton line nearly coincides with an argon line (see, purification of argon), the intensity of which, naturally, does not vanish with decreasing krypton concentration. On the other hand the relative intensity of the same line pair was also determined in the atmospheric rare gases ; the results of these determinations are shown as $y_1 - y_6$ in Fig. 3.

Each $y_n$ is effected with a light error also, as shown in the figure. The horizontal line $\bar{y}$ is the weighted mean of these six determinations, using the reciprocal light errors as weights.

The oblique line is our intensity-concentration scale, the horizontal one represents the intensity corresponding to the unknown concentration : their point of intersection determines the unknown concentration itself : in this case $1\cdot60 \times 10^{-4}$.

Each pair of spectrum lines allows the construction of a graph analogous to Fig. 3 and it gives a value for the unknown concentration of krypton in air-argon. Table I. contains the results of all our pairs of lines. The pair krypton 5871/argon 6279 is mentioned twice, because the experimental conditions were so different in both cases that it seemed improper to unite them in one graph. (The tube current was 2·0 Å. in the first and 0·7 in the second case; the grey glass intensity scale was used in the first and the undoubtedly achromatic " Hansen-Blende " in the second.) It is possible that the very high value of the first determination is due to the insufficient achromacy of the grey glasses.

TABLE I.

| Krypton Line. | Argon Line. | Krypton (vol. conc. $\times 10^{-4}$). |
|---|---|---|
| 5871 Å., $1s_4$–$2p_2$ | 6279 Å., $2p_6$–$5d_4$ | 2·45 |
| ,, ,, | ,, ,, | 1·85 |
| ,, ,, | 5784 Å., $2p_7$–$5s_1$ | 1·50 |
| ,, ,, | 5712 Å., $2p_5$–$7d_5$ | 1·56 |
| ,, ,, | 5701 Å., $2p_6$–$6d_4$ | 1·74 |
| ,, ,, | 5534 Å., $2p_3$–$5s_2$ | 1·44 |
| 4319 Å., $1s_5$–$3p_9$ | 4753 Å., $2p_{10}$–$8d_5$ | 1·38 |
| ,, ,, | 4647 Å., $2p_{10}$–$9d_5$ | 1·36 |
| ,, ,, | 4642 Å., $2p_{10}$–$9d_3$ | 1·29 |
| ,, ,, | 4637 Å., ? | 1·92 |
| ,, ,, | 4237 Å., ? | 1·66 |
| 4464 Å., $1s_4$–$3p_7$ | 4753 Å., $2p_{10}$–$8d_5$ | 1·39 |
| ,, ,, | 4647 Å., $2p_{10}$–$9d_5$ | 1·44 |

To a somewhat rough approximation we calculate the unweighted mean value of krypton concentration from Table I. and arrive at the value $1\cdot6 \times 10^{-4}$ krypton : argon. Knowing the argon content of the air to be 0·935 per cent. the krypton content of the air is

$$1\cdot5 \times 10^{-6} \text{ volume parts.}$$

We estimate the mean error of this determination to be $0\cdot2 \times 10^{-6}$.

A more detailed calculation on the experimental data gave about the same result and allowed the following computation of the mean error. The results of different plates were dealt with separately so that, instead of 13, 36 individual results were obtained. The standard error of each individual result was estimated, assuming that two parallel lines at the distance of the mean deviation from the straight line limit the probable positions of the latter. These limiting scale-lines are intersected by the two limiting intensity ratio values $(Y_n)$ of the atmospheric rare gas mixture and then yield two extreme values for its krypton content, determining a probable interval $(\Delta X_n)$ for the latter. The 36 mean values of these individual experiments are drawn to a distribution curve in Fig. 4. The abscissæ are the krypton concentration of atmospheric argon. The ordinates represent the number of individual results, falling within an interval of $0\cdot4 \times 10^{-4}$ of the abscissæ. It is worthy of note that the maximum of the distribution curve and the calculated mean value coincide fairly well.

   The somewhat large divergence between the individual results is a common feature of quantitative spectrophotometric determinations. The only way to get a precise value is always to make a large number of individual determinations and to calculate a mean value. In spite of this, the photographic method still has all the advantages of being an objective one, as against the visual comparison of very weak spectral lines. The cause of the large divergence must probably be ascribed to inhomogeneity, especially in the thickness, of the photographic layer. W. H. Bandermann[11] only recently investigated this question again, and found that the thickness of the layer varies within a single plate, e.g. from 2·5 to 6·0 mg./cm$^2$.

   Using the $\Delta X_n$ as weights, the mean value of the krypton content of atmospheric argon was calculated to be $1·54 \times 10^{-4}$. The weighted standard error of these 36 determinations was found to be $0·17 \times 10^{-4}$. Multiplying by 0·00935, we finally obtain the *krypton content of the air*:
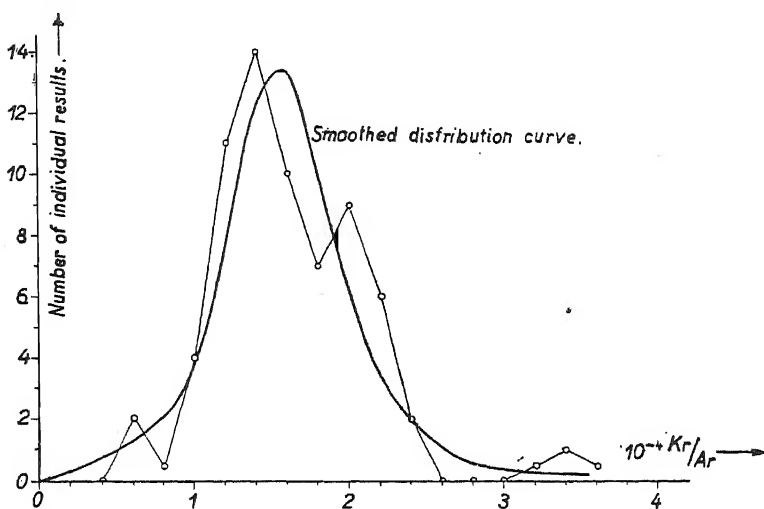


FIG. 4.

$1·44 \times 10^{-6}$ with the standard error of $\pm 0·16 \times 10^{-6}$. This is in sufficient agreement with the more rough estimation mentioned above : $1·5 \times 10^{-6} \pm 0·2 \times 10^{-6}$. Omitting the second decimal we think that latter value is the most adequate mean result of our experiments.

   The value $1·5 \times 10^{-6}$ lies in the same order of magnitude as that of Moureu and Lepape, but exceeds the latter by about 40 per cent. Owing to the fact that our determination is a mean result calculated from a series of quite independent, objective measurements on three different krypton lines we hold our value to be up to the present, the most accurate determination of krypton in the atmosphere.

   *Added in Proof.*—This paper would be incomplete without a brief discussion of two recent communications on the same subject.

   The Linde Gesellschaft kindly submitted to us the galley-proof of a paper by G. Damköhler which is about to appear in Z. *Elektrochemie,* entitled : *Neubestimmung des Krypton und Xenongehaltes der atmosphär-*

[11] W. H. Bandermann, Z. *Physik.*, **90,** 266, 1934.

*ischen Luft.* Damköhler submitted some cubic metres of air, and of liquid oxygen out of air, to a series of fractional distillations followed by fractional adsorptions. He purified the residue chemically and examined the remaining inert gases quantitatively with a gas interfero-meter and by a process of fractional desorption. His mean value for volume parts krypton in the air is $1 \cdot 1 \times 10^{-6} \pm 0 \cdot 1 \times 10^{-6}$, in good agreement with Moureu and Lepape. We explained above that all fractionation methods, which allow large quantities of gas " free from krypton " to escape, are open to criticism and only give a lower limit of the possible krypton concentration. The fact that the final adsorbers in Damköhler's apparatus did not take up any appreciable amount of krypton, does not prove that the enormous volume of the rejected gases did not contain sufficient krypton to account for the difference between our results. Moreover, the interferometric determination of a three-component mixture becomes possible only through Damköhler's hypo-thesis that the X : Kr ratio is 8 : 100, so that ultimately the interferometric data are dependent on the result of the desorption analysis. Blank controls and a detailed description of the desorption analysis would have been very interesting, and we hope that the paper of H. Kahle on this subject will soon explain how the great difficulties of a quantitative desorption analysis were overcome.

Our results are strongly confirmed by the recent paper of F. J. Metzger.[10] He reports that segregation of liquid air on an industrial scale yielded effectively more than $1 \times 10^{-6}$ volume parts of krypton, so that Moureu and Lepape's value must necessarily be too low. Com-bining the fact that *more* than $10^{-6}$ parts were isolated, with Metzger's assumption that 75 per cent. of the krypton was actually recovered, we calculate that $1 \cdot 33 \times 10^{-6}$ volume parts is a *lower* limit.

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# THE EXCITATION OF MOLECULAR VIBRATION BY IMPACT OF SLOW ELECTRONS.

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The excitation of the higher electronic states of atoms and molecules by electron collisions has been studied to a great extent both experi-mentally and theoretically, but the possibility of excitation of nuclear vibration and rotation (unaccompanied by electronic excitation) by collision of electrons with molecules has been investigated to a relatively small extent. This is to be expected, as the methods of experimental investigation of such phenomena are necessarily more difficult to develop, the energy losses suffered by the colliding electrons being comparatively small as well as the frequency of the effective collisions. However, there is now a considerable body of indirect evidence as to the magnitude of

the probability of this type of inelastic collision. Thus, investigations made with the Townsend-Bailey [1] type of apparatus have shown that slow electrons lose energy in collisions with molecules in greater amount than would be expected for purely elastic collisions. Also Harries [2] and Ramien,[3] investigating the passage of slow electrons through nitrogen and hydrogen respectively, have shown that about 1-2 per cent. of the collisions of 3-10 volt electrons with these molecules result in excitation of a single vibrational quantum (*i.e.* in hydrogen an energy loss of $0.54$ volts). On the classical theory one would not, at first sight, expect any such transfer of energy, owing to the small momentum of the incident electron, but Franck and Jordan [4] suggested a mechanism by means of which the transfer could be effected. They suppose the electron to produce disturbance in the binding forces of the atoms in the molecule so setting them vibrating. It is our aim in this paper to obtain theoretical estimates by quantum mechanical methods, of the probability of vibrational excitation in the simplest cases, in order to effect a comparison with experiment.

## General Theory.

The excitation of molecular vibration by the impact of heavy particles has already been considered by several authors,[5] but the electronic case has to be dealt with somewhat differently. Apart from the big difference in the colliding masses, the sign of the field of force acting on the electron is opposite to that acting on the heavy particle, and there is no limit to the distance of closest approach in the classical sense. Before discussing the effect of this difference in detail, let us first consider the formulation of the theory.

The theory of inelastic collisions is not an exact one, so the approximate form of the theory which is most likely to be accurate for any special case must be carefully considered. The simplest form, due to Born,[6] neglects all perturbing effects of the interaction between colliding particle and scatterer in the zero order approximation. The first modification of this method (the method of distorted waves)[7] allows for the perturbation of the initial and final waves representing the relative motion of scattering and colliding particle by their interaction energy averaged over the initial and final states of the internal motions. This modification is essential in dealing with excitation of vibration by heavy particles as, without it, the colliding particles are assumed to penetrate indefinitely, giving a much greater probability than actually exists for any type of inelastic collision. For the case we are considering we shall see that the modification is by no means so important.

Let $(\rho, \zeta, \psi)$ denote the relative polar co-ordinates of the nuclei of the diatomic molecule concerned $(r, \theta, \phi)$ the polar co-ordinates of the incident electron relative to the centre of mass of the molecule. Then the probability of excitation of the $m^{th}$ state of the relative nuclear

[1] Bailey, *Phil. Mag.*, **46**, 213, 1923 ; **50**, 825, 1925 ; **13**, 993, 1932. Bailey and McGee, *Phil. Mag.*, **6**, 1073, 1928 ; Bailey and Duncanson, *Phil. Mag.*, **10**, 145, 1930 Bröse and Saaymen, *Ann. Physik*, **5**, 797, 1930.
[2] *Z. Physik*, **42**, 26, 1927. [3] *Ibid.*, **70**, 353, 1931.
[4] *Anregung von Quantensprüngen durch Stösse*, p. 255, 1926.
[5] Mott and Massey, *Theory of Atomic Collisions*, p. 248, Oxford, 1933.
[6] *Vide ibid:*, pp. 96, 98, Oxford, 1933.
[7] *Ibid.*, p. 100.

motion from the $n^{\text{th}}$ is given, within the range of validity of the method of distorted waves, by,[8]

$$\int_0^\pi \int_0^{2\pi} \frac{k'}{k} \frac{4\pi^2 m^2}{h^4} \left| \iint V(\boldsymbol{\rho}, \mathbf{r}) \psi_n(\boldsymbol{\rho}) \psi_m^*(\boldsymbol{\rho}) F_0(r', \theta') F_1(r', \pi - \Theta) d\mathbf{r}' d\boldsymbol{\rho} \right|^2$$
$$\sin \theta d\theta d\phi \quad (1)$$

where
$$\cos \Theta = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos (\phi - \phi').$$

Here $\psi_n$, $\psi_m$ are the wave functions of the nuclear motion, $V(\mathbf{r}, \boldsymbol{\rho})$ is the interaction energy between the electron and the molecule averaged over the co-ordinates of the molecular electrons. $F_0$, $F_1$ are proper solutions of the equations

$$\left\{ \nabla^2 + k^2 - \frac{8\pi^2 m}{h^2} \int V(\mathbf{r}, \boldsymbol{\rho}) \mid \psi_n(\boldsymbol{\rho}) \mid^2 d\boldsymbol{\rho} \right\} F_0 = 0, \quad . \quad (2)$$

$$\left\{ \nabla^2 + k'^2 - \frac{8\pi^2 m}{h^2} \int V(\mathbf{r}, \boldsymbol{\rho}) \mid \psi_m(\boldsymbol{\rho}) \mid^2 d\boldsymbol{\rho} \right\} F_1 = 0, \quad . \quad (3)$$

which have the asymptotic form of a plane wave of unit amplitude plus a corresponding scattered spherical wave. $k/2\pi$, $k'/2\pi$ are the wave numbers of the motion of the electron relative to the centre of mass of the molecule before and after the impact respectively. If we neglect the terms involving $V(\mathbf{r}, \boldsymbol{\rho})$ in (2) and (3) we obtain Born's approximation, $F_0$, $F_1$ becoming plane waves $e^{ikr \cos \theta}$, $e^{-ik'r \cos \Theta}$ respectively.

If $V$ is a powerful repulsive potential, $F_0$, $F_1$ will differ from the corresponding plane waves by being of much smaller magnitude inside the region of classical closest distance of approach and the distorted wave formula (1) gives a much smaller probability than Born's (by a factor of the order of $10^6$ for gas atoms at ordinary temperatures). For an attractive potential the effect of $V$ is much less marked. It results in a decrease of wave-length in the region in which it is of magnitude greater than, or comparable with, the kinetic energy of the electron, but no very great change in amplitude. It should not, therefore, be a very bad approximation to first use Born's formula for the problem with which we are concerned. This should suffice to obtain an order of magnitude for the probability and the effect of introducing distortion can be considered later. Such a standpoint receives support from a study of electron excitation of atoms. The effect of distortion in this case must be similar to that in the case we are considering, and it is known, from the investigations of Massey and Mohr on the excitation of the $2^1P$ and $2^3P$ states of helium [9] and of Soden on the ionisation of helium,[10] that the inclusion of distortion results in the increase of the calculated probability of excitation by low voltage electrons by a factor of about 2 only.

### Calculations for a Symmetrical Diatomic Molecule.

Let us first assume that the interaction energy $V(\mathbf{r}, \boldsymbol{\rho})$ may be written in the form

$$V(\mid \mathbf{r} - \tfrac{1}{2}\boldsymbol{\rho} \mid) + V(\mid \mathbf{r} + \tfrac{1}{2}\boldsymbol{\rho} \mid). \quad . \quad . \quad (4)$$

The calculations of Hund [11] using the Fermi-Thomas statistical method have shown that this is a sufficiently good approximation if the nuclei

[8] Mott and Massey, *loc. cit.*          [9] *Proc. Roy. Soc.*, **139A**, 187, 1932.
[10] *Ann. Physik*, **19**, 409, 1934.          [11] *Z. Physik*, **77**, 12, 1932.

are at rest. Born's formula gives, then, for the matrix elements associated with the transition from the $n^{th}$ to the $m^{th}$ state

$$\iint [V(|\mathbf{r} - \tfrac{1}{2}\boldsymbol{\rho}|) + V(|\mathbf{r} + \tfrac{1}{2}\boldsymbol{\rho}|)]e^{i(k\mathbf{n_0} - k'\mathbf{n_1})\cdot\mathbf{r}}\psi_n\psi_m^* d\mathbf{r}d\boldsymbol{\rho}. \quad (5)$$

This can be written as the product

$$2\int \cos\{\tfrac{1}{2}(k\mathbf{n_0} - k'\mathbf{n_1})\cdot\boldsymbol{\rho}\}\psi_n(\boldsymbol{\rho})\psi_m^*(\boldsymbol{\rho})d\boldsymbol{\rho} \cdot \int V(\boldsymbol{\sigma})e^{i(k\mathbf{n_0} - k'\mathbf{n_1})\cdot\boldsymbol{\sigma}}d\boldsymbol{\sigma}. \quad (6)$$

To the same approximation the matrix element appearing in the elastic scattering is

$$2\int \cos\{\tfrac{1}{2}(k\mathbf{n_0} - k\mathbf{n_1})\cdot\boldsymbol{\rho}\}|\psi_n(\boldsymbol{\rho})|^2 d\boldsymbol{\rho} \cdot \int V(\boldsymbol{\sigma})e^{i(k\mathbf{n_0} - k\mathbf{n_1})\cdot\boldsymbol{\sigma}}d\sigma, . \quad (7)$$

so the probability that the $m^{th}$ state should be excited is determined mainly by the ratio of

$$\left|\int \cos\{\tfrac{1}{2}(k\mathbf{n_0} - k'\mathbf{n_1})\cdot\boldsymbol{\rho}\}\psi_n(\boldsymbol{\rho})\psi_m^*(\boldsymbol{\rho})d\boldsymbol{\rho}\right|^2,$$

to unity if the energy loss is small compared with the incident energy. Since $\psi_n$, $\psi_m$ are orthogonal, this ratio is small, and if $\tfrac{1}{2}(k\mathbf{n_0} - k'\mathbf{n_1})\cdot\boldsymbol{\rho}$ is small for such values of $\boldsymbol{\rho}$ that the functions $\psi$ are of appreciable magnitude, *i.e.* if the wave-length of the incident electron is large compared with the nuclear separation, the probability will be very small indeed, certainly much too small to be detected in the experiments cited in the introduction. This shows that it is not correct to assume that $V$ is simply a function of the distances of the electron from the nuclei, and does not depend explicitly on the nuclear separation. The inclusion of some terms involving the nuclear separation explicitly can have a considerable effect on the probability. Thus, writing

$$V = [v(|\mathbf{r} + \tfrac{1}{2}\boldsymbol{\rho}|) + v(|\mathbf{r} - \tfrac{1}{2}\boldsymbol{\rho}|)]v_1(\boldsymbol{\rho}), \qquad . \qquad . \quad (8)$$

we obtain in place of (6)

$$2\int \cos\{\tfrac{1}{2}(k\mathbf{n_0} - k'\mathbf{n_1})\cdot\boldsymbol{\rho}\}v_1(\boldsymbol{\rho})\psi_n(\boldsymbol{\rho})\psi_m^*(\boldsymbol{\rho})d\boldsymbol{\rho}.$$

If now $v_1(\boldsymbol{\rho})$ has a suitable form, the integral will not vanish when the cosine tends to unity and we can expect a much greater value of the probability for low velocities of impact. The inclusion of a term such as $v_1(\boldsymbol{\rho})$ is essentially similar to Franck and Jordan's classical theory of the process.

Applying the theory to collisions of slow electrons with nitrogen and hydrogen, we take

$$V = Ae^2\left\{e^{-2N|\mathbf{r} - \tfrac{1}{2}\boldsymbol{\rho}|}\left(N + \frac{\alpha}{|\mathbf{r} - \tfrac{1}{2}\boldsymbol{\rho}|}\right) + e^{-2N|\mathbf{r} + \tfrac{1}{2}\boldsymbol{\rho}|}\left(N + \frac{\alpha}{|\mathbf{r} + \tfrac{1}{2}\boldsymbol{\rho}|}\right)\right\}, \quad (9)$$

where $N$, the effective nuclear charge, is not a *constant* but is a function of the nuclear separation $\rho$. In the region of importance, near the equilibrium separation $\rho = \rho_0$ we may expand $N$ in the form

$$N = N_0 + \left(\frac{\partial N}{\partial \rho}\right)_{\rho = \rho_0}(\rho - \rho_0) + \cdots$$

and, neglecting $\dfrac{\partial^2 N}{\partial\rho^2}$ and higher derivatives we have, approximately

$$
\begin{aligned}
V = \ &Ae^2\, e^{-2N_0|\mathbf{r}-\frac{1}{2}\boldsymbol{\rho}|}\Big\{N_0 + \frac{\alpha}{|\mathbf{r}-\frac{1}{2}\boldsymbol{\rho}|} \\
&+ (\rho-\rho_0)\Big(\frac{\partial N}{\partial\rho}\Big)_{\rho=\rho_0}(1 - 2\alpha - 2N_0|\mathbf{r}-\tfrac{1}{2}\boldsymbol{\rho}|)\Big\} \\
&+ Ae^2\, e^{-2N_0|\mathbf{r}+\frac{1}{2}\boldsymbol{\rho}|}\Big\{N_0 + \frac{\alpha}{|\mathbf{r}+\frac{1}{2}\boldsymbol{\rho}|} \\
&+ (\rho-\rho_0)\Big(\frac{\partial N}{\partial\rho}\Big)_{\rho=\rho_0}(1 - 2\alpha - 2N_0|\mathbf{r}+\tfrac{1}{2}\boldsymbol{\rho}|)\Big\}, \qquad . \qquad . \quad (10)
\end{aligned}
$$

which includes terms of the form (8) and leads to an integral

$$
\int \cos\{\tfrac{1}{2}(k\mathbf{n}_0 - k'\mathbf{n}_1)\cdot\boldsymbol{\rho}\}(\rho-\rho_0)\psi_n(\boldsymbol{\rho})\psi_m{}^*(\boldsymbol{\rho})\,d\boldsymbol{\rho},
$$

in the transition matrix.

It remains to choose suitable forms for the wave functions $\psi_n$, $\psi_m$. The most accurate vibrational wave functions which have been given are probably those of Morse,[12] but as they do not include the effect of rotation directly and are rather complicated to use we will adopt the simpler functions given by Fues. He gives

$$
\psi_n = \Big(\frac{\rho}{\rho_0}\Big)^{\alpha-1}\frac{(-1)^k}{\Gamma(k+n+1)}\, e^{-A\rho}L_{k+n}^{(k)}(2A\rho)P_l^m(\cos\zeta)\, e^{im\psi}
$$
$$
\Big\{\binom{k+n}{n}\Gamma(k+1)\Big\}^{-\frac{1}{2}}, \quad (11)
$$

where

$$
\alpha = \tfrac{1}{2} + \frac{1}{\chi}\{1 + \chi^2(l + \tfrac{1}{2})^2\}^{\frac{1}{2}},
$$
$$
A = \frac{1}{\chi\rho_0}[\{1 + \chi^2(l + \tfrac{1}{2})^2\}^{\frac{1}{2}} + \chi(n + \tfrac{1}{2})]^{-1},
$$
$$
k = \frac{2}{\chi}\{1 + \chi^2(l + \tfrac{1}{2})^2\}^{\frac{1}{2}},
$$
$$
L_{k+n}^{(k)}(x) = \frac{\Gamma(k+n+1)}{(-1)^k}\sum_{h=0}^{l}(-1)^{n-h}\binom{h+n}{h}\frac{x^{n-h}}{(n-h)\,!},
$$

$l$ is the rotational quantum number and $\chi = \dfrac{h}{4\pi^2\nu_0 I}$, $\nu_0$ being the fundamental frequency and $I$ the moment of inertia of the molecule. $\chi$ is a quantity of the order of magnitude $10^{-2}$ so, except for large $l$,

$$
\alpha = \frac{1}{\chi}, \quad A = \frac{1}{\chi\rho_0}, \quad k = \frac{2}{\chi},
$$

and the form of the wave function is practically independent of the rotational quantum number. We distinguish the transitions by the magnitude of the change of this quantum number. It is then easy to see that for 3-10 volt electrons in hydrogen only transitions in which the rotational quantum number does not change will take place with appreciable probability. For the wave functions $\psi_n$, $\psi_m$ are large near $\rho = \rho_0$,

*i.e.* for $\rho \simeq \frac{3}{2}a_0$ while, for 7-volt electrons $k = 0\cdot7/a_0$ . $k\rho_0$ is, therefore, not appreciably greater than unity, and the only term in the expansion of

$$\cos\{\tfrac{1}{2}(k\mathbf{n_0} - k'\mathbf{n_1}) . \boldsymbol{\rho}\}$$

in a series of Bessel functions which will have appreciable magnitude near $\rho = \rho_0$ will be the zero order term.   This is associated with the harmonic $P_0$ and will combine with rotational states associated with harmonics of the same order (*i.e.* same rotational quantum number).   For nitrogen $k\rho_0$ is about 1·5 and an appreciable contribution may arise from terms in the expansion of the cosine associated with the second harmonic.

Carrying out the integrations for transitions from the ground vibrational state to the first excited vibrational state, in which the rotational quantum number does not change, we obtain for the probability amplitude associated with scattering of the incident electron through an angle $\theta$ :—

$$\frac{16\pi^2 m e^2 A}{h^2 K (4N_0{}^2 + K^2)^3} \sqrt{\frac{\chi}{2}} \Big[ (4N_0{}^2 + K^2)\{\alpha(4N_0{}^2 + K^2) + 4N_0{}^2\}(K \cos \tfrac{1}{2}Kr_0$$

$$- \frac{2}{r_0} \sin \tfrac{1}{2}Kr_0) - 8N_0\{(1 - 2\alpha)(4N_0{}^2 + K^2)$$

$$- (12N_0{}^2 - K^2)\}\Big(\frac{\partial N}{\partial \rho}\Big)_{\rho = \rho_0} \sin \tfrac{1}{2}Kr_0 \Big], \qquad . \qquad . \qquad . \qquad (12)$$

where $\qquad\qquad\qquad K^2 = k^2 + k'^2 - 2kk' \cos \theta.$

For hydrogen we have $r_0 = \frac{3}{2}a_0$, $\chi = \frac{1}{80}$ and $a_0 N = 1 = A = \alpha$ nearly. To obtain an estimate of $\dfrac{\partial N}{\partial \rho}$ we may use the result obtained by N. Rosen [13] for the variation of effective nuclear charge in hydrogen with nuclear separation, calculated by a variation method.   In the neighbourhood of the equilibrium position his calculations give

$$\frac{\partial N}{\partial \rho} = 0\cdot28/a_0.$$

Integrating over all angles of scattering and substituting numerical values gives, for the 1, 0 → 2, 0 transition in hydrogen, a cross-section $\cdot 03 \ \pi a_0{}^2$.

To the same approximation we obtain for the elastic cross-section a value of $7\pi a_0{}^2$, so this theory predicts that only one in every 230 collisions should be effective in vibrational excitation.   This is somewhat less than the observed number of 1 in 50, but it is of interest to note that, if the variation of effective nuclear charge with nuclear separation were not taken into account, the calculated efficiency of vibrational excitation would be much smaller ($< 1/2000$).

For nitrogen $\dfrac{1}{\chi} \simeq 300$ and this would give an even smaller probability than for hydrogen for the same value of $\dfrac{\partial N}{\partial \rho}$, but it is only necessary for $\dfrac{\partial N}{\partial \rho}$ to be effectively twice as great for nitrogen than for hydrogen in order to give the same order of probability in both cases.   Harries actually found a greater efficiency in CO than in $N_2$.   This may arise from the inequality of the nuclei in the former molecule which introduces terms involving $\sin\{\tfrac{1}{2}(k\mathbf{n_0} - k'\mathbf{n_1}) . \boldsymbol{\rho}\}$ in (6) so the contribution due to

[13] *Physic. Rev.*, **31**, 579, 1928.

first order terms does not vanish. Since $\frac{1}{2}k\rho_0 = 0.7$ for these molecules this contribution may be considerable.

In view of the factor of 5 still remaining between theoretical and experimental probabilities for hydrogen, it is necessary to investigate the errors introduced by neglecting the distortion of the initial and final electron waves by the molecular field.

### Effect of Distortion.

Returning to Section I., it will be seen that the use of plane wave functions for the colliding electron involves neglecting the terms

$$\int V(\mathbf{r}, \boldsymbol{\rho}) |\psi_n(\boldsymbol{\rho})|^2 d\boldsymbol{\rho}$$

and

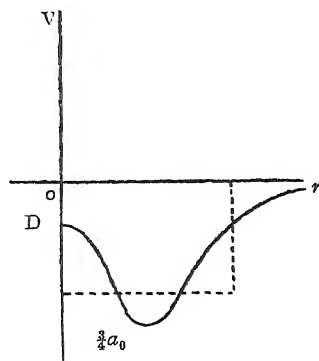$$\int V(\mathbf{r}, \boldsymbol{\rho}) |\psi_m(\boldsymbol{\rho})|^2 d\boldsymbol{\rho}$$



Fig. 1.—Illustrating form of potential acting on incident electron, averaged over all orientations of the molecule, as a function of the distance from the centre of mass of the molecule. Dotted lines indicate approximate potential assumed for purposes of calculation.

in the equations (2) and (3). Now these integrals, which represent the mean potential acting on the incident and inelastically scattered electrons respectively, are functions of the form shown in Fig. 1, and differ very slightly. It is impossible to solve the equations (2) and (3) exactly with the correct form for the integrals, but it

will suffice for our approximation to substitute an approximate form of potential shown in Fig. 1 by the dotted line, *viz.*,

$$\left. \begin{aligned} \int V(\mathbf{r}, \boldsymbol{\rho}) \,|\psi_n(\boldsymbol{\rho})|^2 d\boldsymbol{\rho} \\ = \int V(\mathbf{r}, \boldsymbol{\rho}) \,|\psi_m(\boldsymbol{\rho})|^2 d\boldsymbol{\rho} \end{aligned} \right\} = \left. \begin{aligned} -D \quad r < r_0 \\ \\ r > r_0 \end{aligned} \right\}, \qquad . \qquad (13)$$

where $r_0$ was taken equal to $\frac{3}{4}a_0$ for hydrogen.

We then find for the appropriate solutions $F_0$ and $F_1$, since only the zero order terms in the expansions of $F_0$ and $F_1$ in spherical harmonics are distorted appreciably as the wave-length of the incident electrons is long compared with molecular dimensions,

$$F_0 = e^{ik\mathbf{n}_0 \cdot \mathbf{r}} + \left\{ e^{i\delta_0} f_0(r) - \frac{\sin kr}{kr} \right\}, \qquad . \qquad (14)$$

$$F_1 = e^{-ik'\mathbf{n}_1 \cdot \mathbf{r}} + \left\{ e^{i\eta_0} f_1(r) - \frac{\sin k'r}{k'r} \right\}, \qquad . \qquad (15)$$

where

$f_0(r) = \sin(kr + \delta_0) \qquad r > r_0; \quad f_1(r) = \sin(k'r + \eta_0). \qquad r > r_0$

$\qquad = \left(1 + \dfrac{\mu^2}{k^2}\right)^{-\frac{1}{2}} \sin \mu r \quad r < r_0; \qquad = \left(1 + \dfrac{\nu^2}{k^2}\right)^{-\frac{1}{2}} \sin \nu r. \quad r < r_0,$

$\delta_0 = \arctan\left(\dfrac{k}{\mu} \tan \mu r_0\right) - k r_0; \quad \eta_0 = \arctan\left(\dfrac{k'}{\nu} \tan \nu r_0\right) - k' r_0,$

$\mu = \left(\dfrac{8\pi^2 mD}{h^2} + k^2\right)^{\frac{1}{2}}; \quad \nu = \left(\dfrac{8\pi^2 mD}{h^2} + k'^2\right)^{\frac{1}{2}}. \qquad . \qquad . \qquad (16)$

On substitution in (1) the integrals may be evaluated by using the expansion

$$\frac{\exp. - 2N|\mathbf{r} - \tfrac{1}{2}\boldsymbol{\rho}|}{|\mathbf{r} - \tfrac{1}{2}\boldsymbol{\rho}|} = (\tfrac{1}{2}r\rho)^{-\frac{1}{2}}\Sigma_n(2n+1)K_{n+\frac{1}{2}}(2Nr)I_{n+\frac{1}{2}}(N\rho)P_n(\cos\widehat{r\rho}), \tfrac{1}{2}\rho < r.$$

The value of $D$ was chosen so the elastic cross-section

$$Q_0 = \frac{4\pi}{k^2}\sin^2\delta_0$$

agreed with the observed value of $8\pi a_0^2$.[14]

Carrying out the numerical evaluation of the lengthy expression obtained on integrating (1) using (14) and (15) for $F_0$ and $F_1$ we find for the cross-section for excitation of a vibrational quantum of $H_2$ by 7 volt electrons, the value

$$0.07\ \pi a_0^2.$$

This value is only slightly less than 1 per cent. of the elastic cross-section $8\pi a_0^2$. We thus obtain reasonable agreement with experiment, this agreement depending essentially on the choice of the interaction energy (10) and partly also on the use of the distorted wave approximation. The effect of the latter is to increase the probability by a factor of about 2 just as for the excitation of atoms by electrons and is to be contrasted with the factor of $10^6$ by which the distorted wave approximation differs from Born's in dealing with room temperature collisions between atoms and molecules.

## Concluding Remarks.

It seems from the above calculations that it may be possible to obtain considerable information regarding interatomic forces in molecules from an experimental study of the excitation of nuclear vibration of the molecules by electrons but the experimental evidence at present available is so meagre that it is not possible to derive much information from it.

In the theory of this paper we have treated the interaction of the molecule and electron as if the electron were acted on by a mean field obtained by averaging over all orientations of the molecule. Actually the electron passes a molecule so quickly that its angular displacement is very small during the collision, and it is doubtful if the procedure of averaging the field is strictly accurate. However, if we treated the molecule as a one-dimensional vibrator with fixed orientation it is unlikely that we would obtain results appreciably different from those described above. Our approximation is virtually the same as that used by Hartree in obtaining the effective field acting on an electron due to neighbouring atomic electrons with azimuthal quantum number greater than unity.

## Summary.

The excitation of molecular vibration in diatomic molecules by electron impact is considered using the quantum mechanical theory of collisions. It is found that, if one allows for the change in the effective nuclear charge of a molecular atom acting on the incident electron as the nuclear separation in the molecule varies and also, if the distorting effect of the molecular field on the incident and scattered electron waves is included, about 1 per cent. of the collisions between a 7-volt electron and a hydrogen molecule result in excitation of a single quantum of vibrational energy. This is in reasonable agreement with the observed value of 2 per cent. effective collisions.

[14] Normand, *Physic. Rev.*, **35**, 1217, 1930.

# THE INFLUENCE OF ADSORBED FILMS ON THE POTENTIAL DIFFERENCE BETWEEN SOLIDS AND AQUEOUS SOLUTIONS, with special reference to the Effect of Xanthates on Galena.

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The potential between a solid conductor and an aqueous solution depends in general on the nature of the solid and the solution, on the current density passing across the interface, and on the presence or absence of adsorbed films. The effect of current density at the interface between metals and solutions has been very extensively studied, especially when the metal is made the cathode, and the conditions governing the " overpotential " at these surfaces are fairly well known. When the metal is *cathodic*, it seems probable that the increase in negative potential of the metal which takes place as the current density is increased can be explained by the distribution of the energy levels of the electrons in the metal, which must be extracted from the metal in order to neutralise the ions, whose discharge at the cathode carries the current.[1] It does not now appear necessary to assume that adsorbed films of hydrogen atoms, or molecules, present an obstruction to the passage of current which causes the potential to rise above the reversible value when currents pass across the surface of a metallic cathode.

Adsorbed films of foreign substances at metallic *cathodes* usually have a small effect on the potential at low current densities, but the effect may increase with larger currents ; the sign of the effect is not always the same. Thus Newbery [2] found that colloids such as dextrin, gelatine, and gum arabic increased the overvoltage at lead, platinum, and mercury cathodes ; Thiel and Breuning [3] found an increase in overvoltage at platinum cathodes on adding strongly capillary active substances such as butyric and heptylic acids, or amyl alcohol ; ethyl ether also had a similar effect. Glasstone,[4] however, obtained a lowering of the potential required to produce visible evolution of gas at a lead cathode, by methyl and ethyl alcohols and acetic acid, but more strongly adsorbed substances such as isobutyl and isoamyl alcohols gave first a decrease and later an increase of overpotential as the concentration was increased. Onoda [5] found that the overvoltage at a mercury cathode increased as the interfacial tension between the mercury and the solution decreased, *i.e.*, as the adsorption at the interface increased.

At *anodes*, however, there is evidence that adsorbed films of oxygen, probably held strongly to the underlying metal by covalent forces, are

[1] *Cf.* Gurney, *Roy. Soc. Proc.*, **134A**, 137, 1931.
[2] *J. Chem. Soc.*, 2419, 1914.  [3] *Z. anorg. Chem.*, **83**, 329, 1913.
[4] *Trans. Faraday Soc.*, **21**, 36, 1925.  [5] *Z. anorg. Chem.*, **165**, 93, 1927.

responsible for a great part of the change in potential caused by changing the direction of current so that the metal becomes anodic instead of cathodic. Glasstone [6] and Kremann [7] have summarised this evidence; more recently Bowden,[8] and Butler and Armstrong,[9] have measured the quantity of electricity which had to be passed in order to bring a sufficient number of oxygen atoms into combination with the metal surface to change the potential from that of a clean metal surface to that of one covered with oxygen.

The potential of reversible electrodes appears usually to be inappreciably affected by the presence of adsorbed films at their surfaces; Freundlich and Rona [10] found practically no effect on the $\epsilon$ or total contact potential of a glass electrode, by the addition of substances which strongly affected the $\zeta$ or electrokinetic " potential." Freundlich and Wreschner [11] found no change in the potential of a calomel half-cell, on adding certain dyestuffs to the solution bathing the mercury, although it was clear from electrocapillary measurements that these dyestuffs were strongly adsorbed at mercury surfaces. In this work we have found almost no change in the potential of a silver-silver chloride electrode on adding amyl alcohol or butyronitrile, the latter being chosen because longer chain nitriles cause a large change in the air-liquid potential when present as insoluble surface films. Also, the generally successful use of reversible electrodes without any special precautions to avoid accidental adsorbed films indicates that such films are rarely, if ever, of importance in influencing the potential.

Galena surfaces have been studied by Kamienski,[12] who found that emulsions of terpineol and xanthates rendered the galena more negative; the state of polarisation was not, however, controlled. In this paper we describe a detailed extension of his work, with control of the polarising current, of the dissolved gases, and of the acidity of the solutions.

## Experimental.

Fig. 1 shows the experimental cell and electrical connections used for most of the experiments. The galena crystal was held in a short length of rubber tubing at A, one face being exposed to the water. The joint was made mercury tight by binding with wire.* Contact with the upper face of the crystal was made with a column of mercury in a glass tube fitting into the upper end of the rubber tube. The vessel B containing the solution communicated via a bent tube C containing a gel of 3 per cent. agar in saturated KCl solution, with a pair of beakers containing saturated KCl, connected by a tube filled with the same solution; a saturated calomel electrode D dipped into the farther beaker. The liquid in B could be changed by a tap at the lower end, fresh solution being run

[6] *The Electrochemistry of Solutions*, chapter 20, 1930.

[7] Wien-Harms, *Handbuch d. Exp. Physik.*, vol. 12, part 2, 224-254, 1933.

[8] *Roy Soc. Proc.*, 125A, 446, 1929.    [9] *J. Chem. Soc.,* 743, 1934.

[10] *Sitzb. Preuss. Akad. Wiss.*, 397, 1920.    [11] *Kolloid Z.*, 28, 250, 1921.

[12] *Nature*, 129, 59, 1932; *Congrès International d'Electricité*, 9, 297, 1932; *Z. physikal. Chem.*, 158A, 441, 1932.

* Electrical leakage from the mercury to the aqueous solution directly is a possible danger, but we do not think any appreciable error has arisen from this cause. It could only occur if a thin film of aqueous solution crept in between the rubber and the galena; the resistance of this would be several thousand ohms, while that of our galena crystals was a few ohms only. In some experiments the inside of the rubber tube was waxed, but we abandoned this as there was risk of some contamination of the galena surface; in others, the galena crystal was fixed into the end of a glass tube with picene, and the joint tested for air-tightness; the results agreed well with those obtained by using the rubber tubing.

in from a reservoir E.  Both D and E were closed with rubber corks, and hydrogen, purified by passing through alkaline pyrogallol followed by $N/$100 KCl,* could be bubbled through to free the solutions from dissolved air.

A tungsten wire F dipped into a second vessel communicating with B ; the connections shown in the upper right-hand part of Fig. 1 provided a means of passing a known small current across the galena-solution interface, to control the polarisation ; this was measured on the galvanometer G.

The potential of the experimental cell was measured with the Lindemann electrometer L, a standard cell S and potentiometer P.  The paraffin block W permitted (1) direct connection of the electrometer needle to earth (2) connection to earth through a standard cell and potentiometer (3) connection to earth through experimental cell including
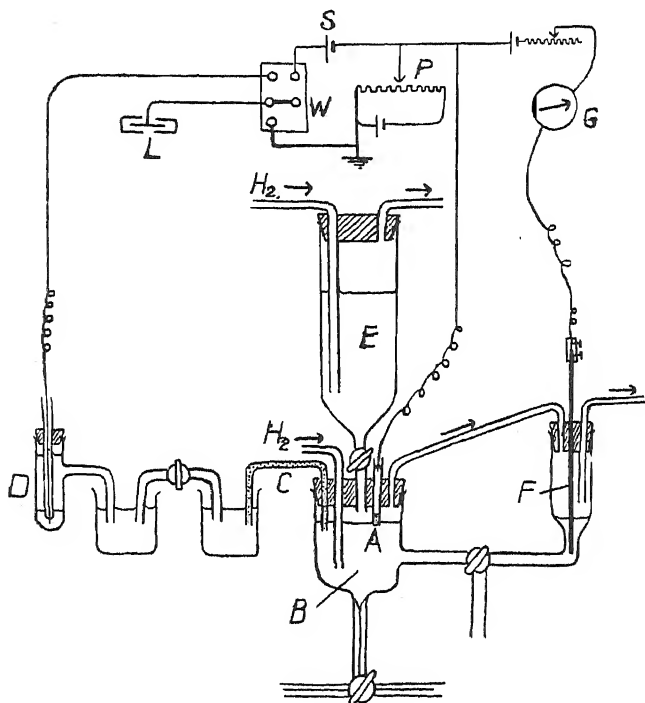


FIG. 1.—Apparatus and electrical connections.

calomel cell and galena, and the potentiometer.  The electrometer was always used as a null instrument, the needle being brought to zero by varying the potentiometer.

Some experiments were also done with the connection to the calomel cell, containing saturated potassium chloride, pressed very close to the galena surface, in order to discover whether any error was introduced into the overpotential measurements through the arrangement illustrated in Fig. 1, in which there is some length of dilute solution between the galena surface and the strong solutions of very high conductivity.  As was expected, there was no difference greater than one millivolt with the maximum polarising current used (a few microamperes).

* In some later experiments a bubbler of mercuric chloride solution was interposed after the pyrogallol.

With the unbuffered solutions, the e.m.f. of the following chain was usually measured

galena/KCl o·oi$N$ + X/KCl sat. in agar/KCl sat./HgCl/Hg
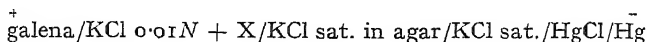
X indicates the added xanthate, the left-hand end being taken as positive ; the e.m.f. of the whole cell is recorded (it is of course negative when the galena is negative with respect to the mercury) ; the potential of the galena on the hydrogen scale can be obtained by adding o·25 volts. In some earlier experiments the saturated calomel half-cell was replaced by one with $N$/100 KCl, and $N$/100 KCl used throughout ; this cell gave readings o·137 volt more negative than the cell with saturated KCl. The saturated solution was preferred as less likely to be affected by changes in the liquid junction potential, when capillary active substances are added to the solution. Any such changes have been assumed to be negligible in comparison with the change at the solid surface.

As galena surfaces oxidise very quickly in the air, when a reduced surface was required, the crystal was cleaved under sodium sulphide solution, washed with the solution to be used in B, and transferred as quickly as possible to the rubber tube ; the polarising current was started as soon as possible and allowed to pass for some time before e.m.f. measurements were taken. If an oxidised surface was wanted, the galena was cleaved in air. The apparent area of the exposed face was usually about o·2 sq. cm. Except where otherwise stated, hydrogen was passed during cathodic measurements and air during anodic. All measurements were made at room temperatures.

The potassium ethyl or butyl xanthates were purified in small quantities shortly before use, by dissolving in alcohol, filtering hot, adding an equal volume of ether and cooling ; the crystals which separated were washed with ether and dried in air.

## Unbuffered Solutions.

The first experiments were done on freshly cleaved galena surfaces, no polarising currents being passed except the very small accidental currents incidental to the use of the electrometer. The potential of such surfaces drifted regularly to more positive values ; the addition of xanthates rendered the galena markedly more negative, but no quantitative result could be obtained owing to the general drift of potential. Fig. 2 shows typical results, the e.m.f. of the cell being plotted against time. Curve 1 has two breaks, separating the three principal parts (a), (b), and (c). Part (a) was taken with the galena in o·oi$N$ KCl, (b) in o·oi$N$ KCl with



FIG. 2.—Potential drift of galena with and without xanthate.

1·326 gm. per litre potassium ethyl xanthate added, and (c) in o·oi$N$ KCl again. In curve 2, (d) was taken in o·oi$N$ KCl, and (e) in o·oi$N$ KCl with 1·207 gm. per litre of potassium butyl xanthate.

Much steadier, and also higher, potentials were obtained with surfaces which had been oxidised by exposure to air ; Fig. 3 shows the effect of successive additions of potassium butyl xanthate. (a) is with o·oi$N$

KCl alone ; (b) with 3·98 gm. terpineol per litre added ; (c) with 0·44 gm. potassium butyl xanthate per litre ; (d) with 1·062 gm., (e) with 5·154 gm., (f) with 10·77 gm. potassium butyl xanthate per litre ; (g) is the final curve when the xanthate solutions were again replaced by 0·01 N KCl. Under the conditions of this experiment, the xanthate does not appear to have been completely washed off the surface. These re-sults on oxi-
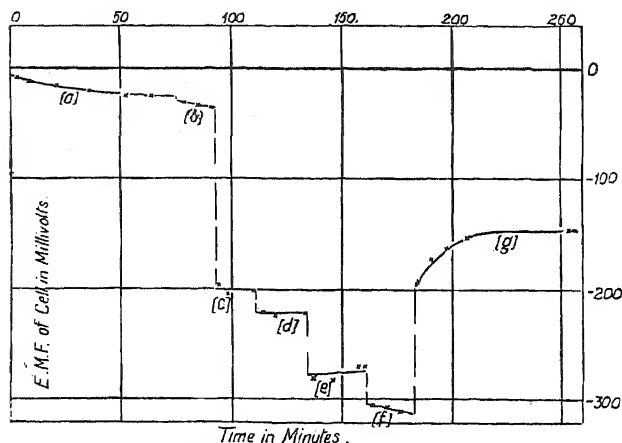


FIG. 3.—Effect of xanthate on oxidised galena.

dised surfaces are generally similar to those obtained by Kamienski [12] on adding an emulsion of xanthate and terpineol to galena ; it is clear that the potential changes are due to the xanthate and not to the terpineol.

Further analysis of the dependence of the potential on conditions was obtained when the polarising current and the atmosphere above the liquid were controlled ; Fig. 4 shows the polarising current, also the approximate current density calculated on the apparent area of the exposed surface of the galena crystal, plotted as abscissæ ; the cathodic currents are shown negative on the left of the diagram and the anodic positive to the right, as will be done throughout this paper.



FIG. 4.—Effect of polarising currents.

The small inset diagrams show the course of the potential-current curves down to quite small currents.

Curve 1 is cathodic in 0·01$N$ KCl in an atmosphere of hydrogen ; curve 3 the same in air ; curve 2 shows the influence of 10·13 gm. per litre of potassium butyl xanthate. At low polarising currents the xanthate causes no change greater than the usual divergence between successive experiments ; the negative overpotential is slightly reduced by the xanthate at polarising currents of 3 microamperes per sq. cm. and over.

With the galena anodic, the atmosphere made no difference to the results, but xanthate lowered the potential very much. Curve 4 shows the potential variation in air and in hydrogen, the crosses and plain dots indicating observations in hydrogen, the ringed dots those in air. Both sets of points lie on the same curve. The anodic current clearly controls the state of oxidation of the surface so strongly that the atmosphere is without effect. In curves 6 and 7, potassium ethyl xanthate to the amounts of 1·03 and 4·96 grams per litre have been added, a considerable fall in potential being produced with the smaller amount and a slight further fall with the larger quantity. Curve 5 shows the potentials obtained after washing out the xanthate with $N$/100 KCl and maintaining the galena anodic in the xanthate-free solution for fifteen hours ; the effect of the xanthate has been completely removed by this treatment.
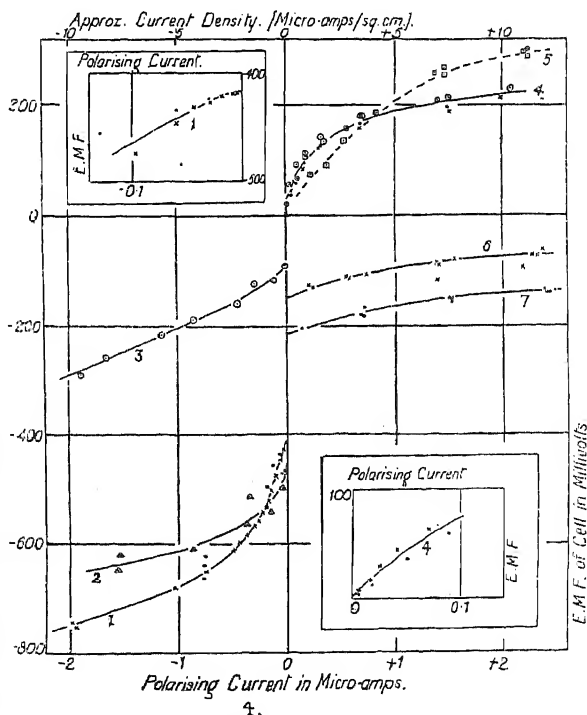
Fig. 5 represents the same data as Fig. 4 with curves numbered to correspond, except that the logarithm to base 10 of the current is plotted as abscissa. There is a linear relationship between the logarithm of the current and the potential, at currents above about 2 × 10$^{-7}$ amperes, $i.e.$, an apparent current density of about 10$^{-6}$ ; at smaller current densities the logarithmic curves cease to be linear.



FIG. 5.—Effect of polarising currents, plotted logarithmically.

The influence of the concentration of the xanthate added on the anodic potential is indicated in Fig. 6, where the potential extrapolated to zero anodic polarising current is plotted against the concentration, in moles per litre, of potassium ethyl xanthate (curve 1) and potassium butyl xanthate (curve 2). Closely similar curves were obtained if the actual potential measured on oxidised surfaces, but in the absence of polarising currents, as in Fig. 3, was plotted against the concentration of xanthate. An emulsion of 5 grams of terpineol per litre of 0·01$N$ KCl gave practically the same potentials as the KCl alone.

The results given above were obtained after the polarising currents had been passed for fifteen minutes, as it was found that the time of passage of the current affected the potentials to some extent. With cathodic surfaces the potentials obtained with increasing polarising currents were less negative than those obtained with decreasing currents. In curve 1, Fig. 4, at 0·75 microamperes, there are three dots above each other ; these represent readings taken 5, 12 and 20 minutes after the
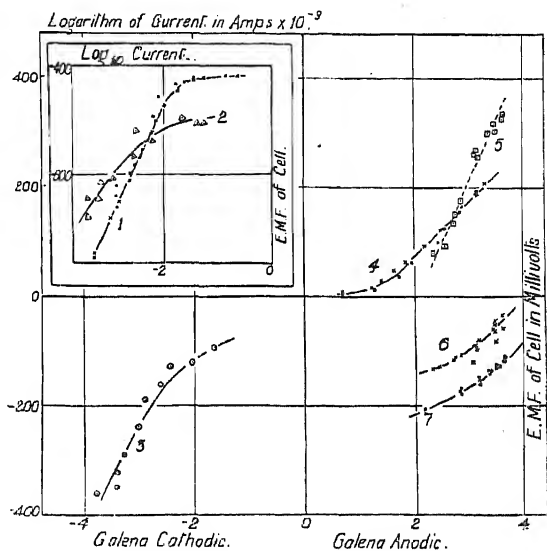
polarising current had been increased suddenly from 0·18 microamperes ; the lowest value is the one at 20 minutes. The change is about 40 millivolts in this time. When a standard time of 15 minutes was adhered to, it was found possible to reproduce the potentials within at most 20 millivolts.

A much longer time was required to obtain steady potentials when changing over from the anodic to the cathodic galena surface, or vice versa. With a constant current of about 3 microamperes per apparent square centimetre about 2 hours was necessary, in one experiment, to establish a steady potential at the typical anodic value for this current, about + 0·16 volts, starting wih a surface which had been cathodically reduced : this is about 0·1 coulombs per sq. cm. Fig. 7 shows the rate at which anodic and cathodic overpotentials were established in another experiment ; on the right, a freshly cleaved galena surface, after a period of cathodic reduction, was made the anode; a small quantity of current was passed at 0·7 microampere per sq. cm., until $10^{-4}$ coulomb per sq. cm. had been passed ; then 15 microamperes per sq. cm. were passed until the final steady oxygen potential was reached. The current was then reversed, using 1·85 microamperes per sq. cm. until $7 \times 10^{-4}$ coulomb had passed, thereafter 15 microamperes per sq. cm., and the change of potential is shown on the left of Fig. 7. About 0·1 coulomb per apparent sq. cm. is necessary to establish the full oxygen overpotential and about half that quantity to establish the hydrogen potential. If the logarithm of the quantity of electricity passed is plotted against the potential, the curves are both very nearly straight lines.



FIG. 6.—Effect of xanthate concentration.

Without much more experiment to determine whether the curves of Fig. 7 are typical, or whether the intensity of current passing or other conditions affect the course of the change from a reduced to an oxidised surface, it would be premature to discuss the meaning of the curves in detail ; especially as the ratio of the real to the apparent surface has not been determined. There are, however, some marked differences between the behaviour of galena electrodes and of platinum, as described by Bowden [8] and by Butler and Armstrong.[8]  First, the quantity of electricity which must be passed to form or destroy the oxidised layer on the surface is 30 to 50 times that required for platinum. Second, there is no break in the curve at any potential intermediate between the hydrogen and oxygen potentials, which Bowden ascribes to the reversible potential of platinum covered with a layer of oxide. Third, the relation between potential and quantity of electricity passed is logarithmic with galena, while Bowden found it accurately linear. Bowden, however, used much larger currents ; Butler and Armstrong did not obtain accurately linear

curves, with currents of the same order of magnitude as those used here.

If we assume that the real area of the galena is five times the apparent area, a reasonable ratio for surfaces possessing a fair degree of polish such as freshly cleaved galena actually shows, it may be calculated from the known crystal lattice of galena that the amount of oxygen required to convert every surface lead and sulphur atom into lead sulphate could be liberated by the passage of $10^{-3}$ coulombs of electricity per apparent sq. cm., and a similar amount of electricity would be necessary to reduce a monomolecular layer of lead sulphate to sulphide. 50 to 100 times this quantity actually has to be passed to convert the surface from a reduced to an oxidised state, and it is clear either that the efficiency of the electrochemical process is very small, or that the oxidised layer has to be many molecules thick to give the maximum potential. It seems possible that the oxidised surface may be formed, not by a direct electro-chemical process, but by the formation of a layer near the surface rich in oxygen atoms or molecules, of which a few molecules then oxidise the
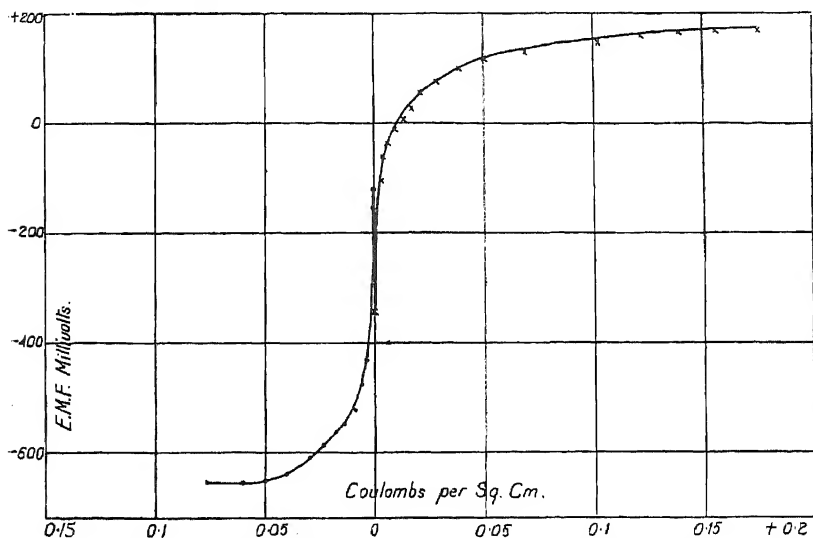
FIG. 7.—Rates of growth of anodic and cathodic potentials.

surface. Much more work will, however, be required to discover the mechanism of formation of the oxidised layer. That there is an oxidised layer, except when the galena is carefully reduced in an atmosphere of hydrogen, appears clear from the fact that a small amount of dissolved air produces a large rise in the potential of the galena, and from the fact that xanthate lowers the potential of galena markedly only when the galena has been exposed to mild oxidation (except when the xanthate has decomposed). Since the oxidised layer combines with xanthate, it is probably not pure lead sulphate, but possibly oxide or a mixture of oxide and sulphate.

## Solutions of Controlled Acidity.

Solutions of $p_H$ approximately 1 ($N/10$ hydrochloric acid), 3·0, and 6·0 ($N/20$ phthalate buffers made up to Clark's formulæ) and 9·0 ($N/20$ borate buffer, Clark), were used.

On $N/10$ hydrochloric acid, in the absence of xanthates, the potentials were very near to those of Fig. 4, obtained with $N/100$ KCl. Addition

of xanthate produced no effect at all with anodic currents, almost certainly because the xanthate was very rapidly decomposed under these conditions ; it was noticed that the solutions became milky and lost their power of precipitating copper sulphate. With cathodically polarised galena, xanthates produced a decided lowering of the potential, the curves being shifted practically parallel to themselves to more negative values, by about 0·1 volt with 1 gram per litre of potassium ethyl xanthate, and 0·3 volt with 5 grams per litre.   At the same time, a strongly adherent yellow film appeared on the galena surface.   The potential rose again, but not to its original value, on washing the xanthate solution away with fresh KCl ;   it was not investigated whether very prolonged washing could restore the original potential obtained before xanthate was added.

In the phthalate solution of $p_H$ 3·0, the potentials were somewhat more positive, with cathodic polarisation, than with $N/100$ KCl ; diluting the buffer twenty times brought the potentials close to those found with KCl.   The exact potentials were difficult to obtain, because there was usually a slight drift towards more negative values ; although the current of hydrogen usually employed in taking the cathodic potentials was passed, there may have been a small amount of dissolved oxygen in the solution at first, which would have raised the potentials.   Addition of xanthate lowered the potentials decidedly, though less than with the dilute HCl, about 10 grams per litre being necessary to produce a fall of 0·15 volt.   The same yellow film was formed as with cathodic galena in dilute HCl.   With anodic galena, potassium butyl xanthate produced a decided lowering of potential, about 0·27 volt for 5 grams per litre, but the effect was rather less than with KCl.

The striking novelty with these two acid solutions is the lowering of potential with cathodic galena, and the formation of the yellow film. It seems probable that this film is formed by decomposition of the xanthate, but its precise nature was not further investigated.

With the phthalate solution of $p_H$ 6·0, and the borate solution of $p_H$ 9·0, on the cathodic side, xanthate produced no effect other than a slight diminution of the rate of increase of negative overpotential with increasing currents ;   the potentials with and without xanthate were much the same as in $N/100$ KCl, but the changes of potential with polarising current were rather smaller.   On the anodic side, an unusually long time seemed to be necessary to produce the typical anodic potential, but eventually nearly the same potentials as with $N/100$ KCl were reached.   Xanthates. lowered the potential not quite so much as in KCl.

On the whole there is no very great difference between the results with the buffered solutions and the unbuffered potassium chloride ; there may be slight specific effects of the buffers in diminishing the influence of the polarising current on the negative overpotential, on the cathodic side ; and on the anodic side, xanthate appears to have slightly less effect than in KCl.

## Galena as a Reversible Electrode.

In sodium sulphide of sufficient strength it was found that galena behaved almost as a reversible electrode.   In an approximately molar solution of sodium sulphide, without any polarising current and with hydrogen bubbling through the solution, the potential was constant with time, as indicated in curve 1 of Fig. 8.   Xanthate had no influence on the potential ;   the crosses indicate potentials with no xanthate present ; the ringed dots those with about 1 gram per litre of potassium ethyl xanthate, and the squared dots with a similar quantity of potassium butyl xanthate.   Curves 2 and 3 are in the same sulphide solution diluted ten and a hundred times respectively, with xanthate added in the same quantity, as indicated by the change in type of the points.   The sudden rises in curve 3, occurring where the solutions were changed, are probably

due to slight oxidation of the galena surfaces by air, the amount of sulphide being insufficient to restore the normal sulphide condition of the surface instantaneously.

The effect of polarising currents was quite small, and is shown in Fig. 9, curves 1, 2, and 3, which are for the approximately molar, tenth molar, and hundredth molar solutions of sodium sulphide. Anodic currents are to the right, cathodic to the left of the middle line. The anodic and cathodic portions of the curves are all continuous, showing that there is no formation of an oxidised layer on the surface; the change of potential as the polarising current changes is quite small with the molar solution, and somewhat larger with the more dilute solutions. Dilution of the solution brings the potential



FIG. 8.—Galena in sodium sulphide.

of the galena to more positive values, about 50 or 60 millivolts for a tenfold dilution, as would be expected if the galena electrode is reversible with respect to the sulphide anion.

In an attempt to obtain a chemically produced oxidised layer on the galena surfaces, they were studied in an acid solution of iron alum. Curves 4, 5, and 6 of Fig. 9 show the potentials with solutions containing 0·1 N sulphuric acid and 24 grams per litre of iron alum, and one-tenth and one-hundredth of these concentrations in both constituents respectively. The potentials are very high, of the same order as those for oxidised galena surfaces; cathodic currents do not remove the oxidised layer in the strengths used, though there is, in the more dilute solutions, a moderate change of potential with current.
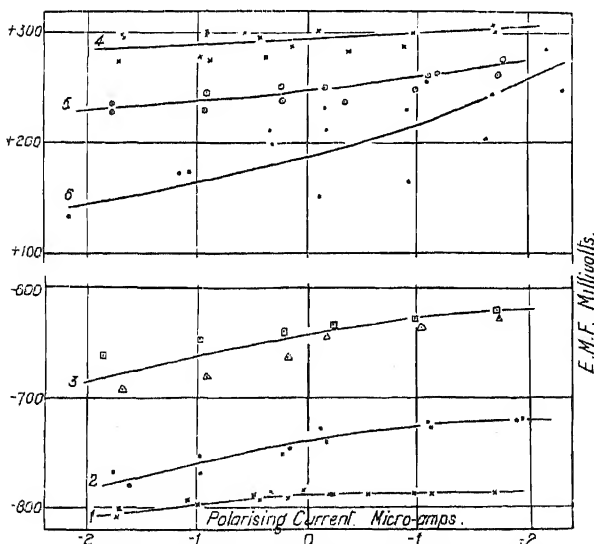


FIG. 9.—(Lower) in sodium sulphide; (upper) in iron alum.

At first it was thought possible that the electrodes were covered with a layer of lead sulphate, which rendered them nearly reversible with respect to the sulphate ion; but the effect of dilution is to render the galena more negative, which is in the wrong direction for this and indicates reversibility with respect to the cation. Tenfold dilutions produced a change of about 55 millivolts, in the above direction.

In sulphuric acid, the galena was not reversible and behaved much

as it did in potassium chloride. In ferric chloride solution, the galena was reversible, showing potentials close to those observed in iron alum ; the sign of the change of potential on dilution indicated reversibility with respect to the cation.

It is not easy to see why a galena electrode should be reversible with respect to ferric ions in solutions ; this effect is being investigated further.

## Experiments with Silver-Silver Chloride Electrodes.

A few measurements were done to discover whether any considerable change occurred in the potential of a silver-silver chloride reversible electrode on the addition of substances likely to be adsorbed. The electrodes were prepared by anodic treatment of silver wire in dilute sodium chloride solution, and used in place of the galena electrodes in the apparatus shown in Fig. 1, but with $N/100$ KCl in the calomel electrode. Iso-amyl alcohol lowered the e.m.f. of the cell by 2 millivolts in a concentration of 5·84 grams per litre ; butyronitrile (7 grams per litre) by 9 millivolts at first, falling by a further 5 millivolts during 20 minutes. These changes are very small in comparison with those obtained by spreading insoluble nitriles or alcohols at air-liquid surfaces, and it is not impossible that they are partly due to changes at the liquid junction caused by addition of the capillary active substances to one of the liquids.

## Summary.

The electrode potential of galena in aqueous solutions has been measured under a variety of conditions. There is a difference of at least 0·4 volt between the potential of fully reduced and oxidised galena surfaces ; plus a considerable overpotential with both anodic and cathodic polarising currents. Oxidised galena is rendered much more negative by adsorption of xanthates on the surface ; the potential of reduced galena surfaces is little affected by xanthate, except in acid solutions, when the xanthate decomposes, leaving a film on the surface.

In sodium sulphide solution, galena forms a reversible electrode with respect to the sulphide ion ; it is not easily oxidised in this solution. Xanthates do not affect the potential of galena when acting as a reversible electrode.

# THE POTENTIOMETRIC TITRATION OF NON-AQUEOUS SOLUTIONS APPLIED TO AMINO ACIDS.

By A. G. Ogston and J. F. Brown.

The present work was undertaken in order to throw fresh light on the nature of amino-acids in solution, through a determination of the effect of change of medium on their dissociation constants. Measurements were made at first in solutions of methyl alcohol, and later extended to solutions in mixtures of ethyl alcohol and water. The results are in general accord with the work of Neuberger.[13]

Brønsted [1] has shown that the concept of acid and bases should be enlarged to include any system in which a proton may be given up by one molecule to another. All ionisation of acids or bases in solution is due to a double acid-base equilibrium, the solvent functioning as a base or acid respectively. The dissociation constants in common use belong in reality to a particular system of this sort, and not to any one substance; one constant only is necessary, and in the general system represented by

$$HA + M \rightleftharpoons A + MH$$

(HA being the acid solute, M the medium base) is defined by

$$K = \frac{[A][MH]}{[HA]}$$

the square brackets representing concentrations.

Such a function is not in fact constant. It is possible, however, to correct the stoichiometric constant $K$ by the substitution for concentrations of activities defined within the system in question; the usual convention defines the activity as approaching the concentration numerically as the concentration of solute in the system approaches zero. This function is convenient in many cases since, when corrected for the activity coefficient, it gives a measure of the extent to which the solute is ionised.

We define $$K_A = \frac{[A][MH]}{[HA]} \times \frac{fA \cdot fMH}{fHA}.$$

The degree of ionisation of an acid is chiefly determined by three factors; first, the electrical work of separating the proton from it, which will depend on the charge type of the acid and the physical properties of the medium; secondly, the " chemical " work of removing the proton; thirdly, the work of combination of the solvent with the proton. Thus for a series of acids, the changes of ionisation produced by a change of medium are primarily typical of their charge types, the other factors being the same for all. The investigation of changes of ionisation in two media can throw light on the charge types of acids.

### Method of Determination.

Potentiometric methods afford the most convenient means for the investigation of acid-base equilibria, and the method of potentiometric titration was adopted in this work.

The interpretation of the data obtained is not without difficulty: the cell employed consists of an electrode reversible to hydrogen in the acid solution, and a standard electrode in its own solution of constant composition, together with a junction of some sort between the two liquids. The potential of the cell gives a measure of the free energy of the whole process, including the reversible removal of hydrogen ions from the acid solution, anions from the solution in the standard cell, and irreversible diffusion or transport of ions of all sorts present across the phase boundary. The potential is only proportional to the logarithm of the product of the acid concentration and its activity coefficient in the half-cell so long as the free energy changes at the phase boundary and at the standard electrode remain constant, and independent of the

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[1] Brønsted, *Chem. Rev.*, 5, 231, 1928.

composition of the solution under investigation. This condition appears to be approximately fulfilled in certain circumstances.

**Determination of Dissociation Constants from Titration Curves.**—Neglecting activity coefficients the form of the " ideal " titration curve is given by

$$K_A = \frac{[H][A]}{[HA]} \qquad . \qquad . \qquad . \qquad . \quad (1)$$

or

$$\log H = \log K_A - \log \frac{[A]}{[HA]} \qquad . \qquad . \qquad . \quad (2)$$

Actual curves deviate more or less from this form. A more strict treatment is possible : the equilibrium condition is given by (1) ; in the case where the titrand is a base in its initial state, and the titrant a strong acid :—

Let

$A =$ conc. of *titrand* in solution in its basic form.

$HA =$ conc. of *titrand* in solution in its acid form.

$M =$ total conc. of *titrand*.

$X =$ conc. the added titrant would have if no reaction had occurred.

$K_M =$ ionic produce of the medium.

At any point the excess of hydrion over the solvent base (hydroxyl in the case of water) is given by

$$H - \frac{K_M}{H} = X - HA \qquad . \qquad . \qquad . \qquad . \quad (3)$$

whence from (1) and (3)

$$\log K_A = \log H + \log \left( \frac{M - X + H - K_M/H}{X + K_M/H - H} \right) \qquad . \quad (4)$$

When the initial state of the titrand is acid and the titrant is a base,

$$\log K_A = \log H - \log \left( \frac{M - X - H + K_M/H}{X + H - K_M/H} \right) . \qquad . \quad (5)$$

To make these equations completely rigid it is necessary to insert the activity coefficients.

In equations (4) and (5) all quantities are known except $K_A$. The dissociation constant can thus be calculated from any point on the curve, irrespective of its form. This method of calculation has been used throughout the present work.

The dissociation constants of substances which are not sufficiently soluble in either acid or basic form can be determined provided that the solubility of the undissolved form is known. Titration can be performed with excess of the solid in solution during a part of the titration. The equilibrium equations become

$$K_A = \frac{[H][A]}{S} \qquad . \qquad . \qquad . \qquad . \quad (6)$$

where the acid is undissolved,

$$K_A = \frac{[H]S}{[HA]} . \qquad . \qquad . \qquad . \qquad . \quad (7)$$

where the base is undissolved, $S$ representing the solubility of the undissolved form. These lead to equations for the titration curve in presence of excess of solid :

$$\log K_A = \log H + \log \frac{S}{X - H + K_M/H} \qquad . \qquad . \quad (8)$$

where the titrand is undissolved base,

$$\log K_A = \log H - \log \frac{S}{X + H - K_M/H} \qquad . \qquad . \quad (9)$$

where the titrand is undissolved acid.

As the titration proceeds in each case the less soluble form is converted to the more soluble, and at the point where there is no solid left in solution the curve undergoes a sharp transition to one of the forms described by (4) and (5).

These equations apply to titrands having only one dissociation constant ; equations describing the course of titration of substances having more than one dissociating group are more complex in character. But where the constants of the different groups are sufficiently different, each region of the curve is described accurately by the appropriate one of the equations given. The constants of most ampholytes of the amino acid class differ sufficiently for this purpose, and each region of the curve approximates closely to the form demanded by a single dissociation constant.

## Experimental.

The Cell.—The use of a cell consisting of two Hildebrand hydrogen electrodes, one in a standard solution of acid in methyl alcohol, was quickly abandoned. The standard adopted was a silver-silver chloride electrode in a half-cell containing a standard solution of sodium chloride in methyl alcohol. The titration half-cell was of the form shown (Fig. 1). The hydrogen bubbles were found to effect stirring very efficiently and no mechanical stirrer was necessary.

Solutions of hydrogen chloride and of potassium methylate in methyl alcohol used for the titrations, were added from burettes through the hydrogen exit tube.

The Liquid Junction.—It is desirable that the liquid investigated should be stirred as nearly up to the junction as possible without seriously disturbing it. A simple junction cannot, therefore, be used. The capillary of the titration half-cell was filled up to the tap with the bridge solution (saturated potassium iodide in



FIG. 1.

methyl alcohol), the bore of the tap being tightly packed with clean cotton wool. The junction between the titrated solution and the bridge solution was thus made in the cotton wool ; very little diffusion occurred and the
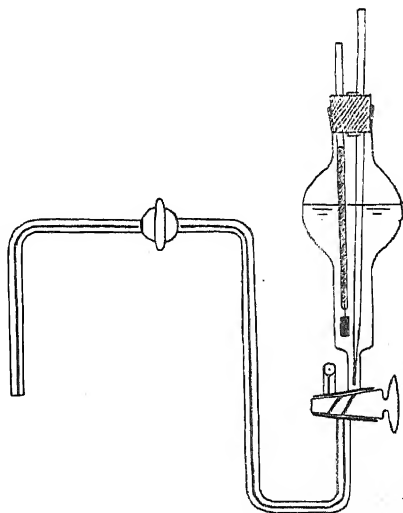
junction appeared to be reproducible to within 2 mv. so long as it was renewed before each run.

The tube from each half-cell passed through a cork into a small vessel containing the bridge solution. Thus the whole apparatus is closed to the air except for the hydrogen exit.

In solutions of aqueous ethyl alcohol the standard electrode was a saturated aqueous calomel and the bridge solution saturated aqueous potassium chloride. The liquid junction was made as before.

## Materials.

The **methyl and ethyl alcohols** used were prepared for conductivity measurements by the method described by Hartley and Raikes [2] and Murray-Rust and Hartley [3] respectively and contained not more than 0·03 per cent. of water.

**Sodium Chloride** was obtained from Merck and twice recrystallised from water.

**Hydrogen Chloride** solutions were made by passing HCl gas, generated from dried B.D.H. A.R. NaCl and pure concentrated $H_2SO_4$ and filtered through glass wool, direct into conductivity MeOH. The strength of the solutions was determined by titration with standard aqueous baryta using bromthymol blue. Solutions were used within twenty-four hours of making.

**Potassium Methylate** solutions were made by shaking conductivity MeOH with potassium amalgam prepared electrolytically : estimated with bromothymol blue against standard aqueous HCl, and diluted as required.

**Hydrogen** was taken from a cylinder, passed over red-hot copper turnings and through concentrated sulphuric acid ; no trouble from impurities was experienced.

**Ammonia** solutions were made by passing ammonia gas, prepared from ·880 ammonia on solid potash and dried with lime, into methyl alcohol.

**Chloracetic Acid** was B.D.H. A.R. recrystallised from benzene, centrifuged and dried.

**Glycine** was B.D.H. A.R. recrystallised from water.

**Tyrosine** was purified by recrystallisation from water.

**Potassium Iodide** was B.D.H. A.R. used without further purification

## Electrodes.

**Silver-silver Chloride Electrodes** (Nonhebel and Hartley) [4] were prepared by silver plating clean platinum gauzes, and chloridising in a solution of $N/10$ NaCl in methyl alcohol. They were found to maintain a potential constant within 2 mv. over a period of a week, if protected from light by wrapping the half-cell in tinfoil.

**Hydrogen Electrodes :** electrodes of iridized gold were first tried ; it has been claimed that they come more rapidly to equilibrium than platinum electrodes (Lewis, Brighton and Sebastian).[5] It was found however, that though they were reasonably satisfactory in acid solutions, they poisoned very rapidly in alkaline solution.

Eventually platinised-platinum electrodes were used according to the directions of Popoff, Kunz and Snow.[6]

It was found that this treatment preserves the full activity of the electrode over a prolonged period without replatinising becoming necessary ; one electrode proved entirely satisfactory for thirty runs.

[2] Hartley and Raikes, *J.C.S.*, **127,** 524, 1925.
[3] Murray-Rust and Hartley, *Proc. Roy. Soc.*, **126A**, 84, 1929.
[4] Nonhebel and Hartley, *Phil. Mag.*, **1,** 729, 1925.
[5] Lewis, Brighton and Sebastian, *J.A.C.S.*, **39**, 2245, 1917.
[6] Popoff, Kunz and Snow, *J. Physic. Chem.*, **32**, 1056, 1928.

The potentials became constant within a period of five to twenty-five minutes ; the controlling factor is probably the removal of dissolved oxygen.

**Measurement of Potentials** was made with a Cambridge Instrument Company standard slide-wire potentiometer with a sensitive mirror galvanometer. No attempt was made to measure to a greater accuracy than 1 mv.

**Temperature.**—A thermostat was not employed but the room temperature was kept within 1 degree of 17° C.

**The Solubility of Tyrosine** in the various solvents was measured colorimetrically by means of Folin's reagent by Mr. J. St. L. Philpot. A saturated solution was made in each case in the solvent in question, filtered, weighed and evaporated to dryness. The tyrosine was dissolved in 10 c.c. $N$ HCl, diluted to 100 c.c. and estimated.

SOLUBILITY OF TYROSINE (gm. mols./litre).

| Water. | 80 Per Cent. EtOH. | 95 Per Cent. EtOH. | MeOH. |
|---|---|---|---|
| $1·45 \times 10^{-3}$ | $3·97 \times 10^{-4}$ | $1·73 \times 10^{-4}$ | $3·93 \times 10^{-4}$ |

## Results.

The titrations were carried out where possible at concentrations of about $N/10$ ; only in the case of glycine in aqueous alcohol were lower concentrations used, owing to its low solubility. The results are not given in full, but a specimen run is given (Table I.) to illustrate the methods of

TABLE I.

### Run 18b.   Methyl Alcohol.

10 c.c. $0·0940N$ anthranilic acid + $3·1$ c.c. $0·0819N$ HCl titrated with $0·0879N$ KOMe. Total volume at neutral point = $15·8$ c.c. Both $H$ and $K_m/H$ are negligible throughout.

| Excess KOMe cc. | $X \cdot 10^3$. | Total Vol. | $M \cdot 10^3$. | $E$. | $p_H$. | $\log \dfrac{M-x}{x}$. | $\log K_A$. |
|---|---|---|---|---|---|---|---|
| 0·06 | — | 15·9 | — | 0·507 | 7·25 | — | — |
| 0·24 | 1·31 | 16·0 | 58·5 | 0·542 | 7·88 | −1·64 | −9·52 |
| 0·50 | 2·69 | 16·3 | 57·6 | 0·562 | 8·20 | −1·31 | −9·51 |
| 1·54 | 7·84 | 17·3 | 54·3 | 0·592 | 8·72 | −0·77 | −9·49 |
| 2·99 | 14·0 | 18·8 | 50·0 | 0·613 | 9·08 | −0·41 | −9·49 |
| 4·56 | 19·7 | 20·4 | 46·0 | 0·629 | 9·38 | −0·13 | −9·51 |
| 6·21 | 24·8 | 22·0 | 42·7 | 0·644 | 9·62 | +0·14 | −9·48 |
| 7·62 | 28·6 | 23·4 | 40·1 | 0·659 | 9·90 | +0·40 | −9·50 |
| 9·25 | 32·4 | 25·1 | 37·4 | 0·681 | 10·27 | +0·81 | −9·46 |
| 9·78 | 33·5 | 25·6 | 36·7 | 0·695 | 10·50 | +1·02 | −9·48 |
| 10·42 | — | — | — | 0·726 | 11·00 | — | — |
| 10·94 | — | — | — | 0·863 | 13·40 | — | — |

Mean : $\log K_A = -9·49$.

calculation and the consistency of the calculated constants ; the constants obtained are summarised in Tables II. to IV. and are in most cases the mean of several runs ; the $pK_A$ values obtained from different runs seldom differed by more than 0·1.

Some of the titration curves are shown (Figs. 2 to 5), plotted on different concentration scales where necessary, to allow a direct comparison. The corrected curves for tyrosine (Fig. 6, shown dotted) show the course which

TABLE II.

| | − log $K_A$. | | Δ( − log $K_A$.) |
|---|---|---|---|
| | Water. | Methyl Alcohol. | |
| Chloroacetic acid . . | 2·8 | 7·4 | 4·6 |
| Ammonia . . . . | 9·1 | 11·4 | 2·3 |
| Anthranilic acid: Function { Acid . . | 5·0 | 9·5 | 4·5 |
| Base . . | 2·0 | 3·5 | 1·5 |
| Tyrosine: Function { Acid . . | 8·4 | 11·7 | 3·3 |
| Base . . | 2·5 | 6·1 | 3·6 |

titration would follow if no solid had separated. The interesting observa-tion was made that, when solid first begins to separate, it does so slowly ; the potential takes some time to reach its final value, starting as though the point lay on the corrected curve and finally reaching the point on the actual curve. This is presumably due to supersaturation ; tyrosine ap-pears to form colloidal solutions readily.

In some runs small amounts of phenol phthalein or of thymol phthalein were added to the cell in order to find approximately the effect produced



by change of solvent on their turning points. The results are shown on the curves of tyrosine and glycine and show the importance of this effect.

## Discussion.

### Determination of $p_H$.

The scales of $p_H$ adopted must be arbi-trary in the absence of any absolute acti-vity standard. Those adopted have been taken with reference to the activity defined within the particular solvent ; the point of reference in each case was $N/10$ hydrogen chloride, the activity coefficient being put equal to unity in the case of aqueous alcoholic solutions in the absence of any knowledge of the values of activity coefficients in these solvents.

If the liquid junction potential remains constant throughout the range of $p_H$, it is sufficient to obtain a relation between $p_H$ and the ob-served potential by drawing a straight line of requisite slope through a single point. In the case of methyl alcohol solutions the data are available for checking its constancy.

FIG. 2.—Glycine + acid :
80 per cent. EtOH ⊙, 95 per cent. EtOH ⊡.

TABLE III.

|  |  |  |  |  | $-\log K_A.$ |  |  | $\Delta(-\log K_A.)$ Water $-95\%$ EtOH: |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | Water. | 80% EtOH. | 95% EtOH. |  |
| Tyrosine: Function | Acid | . | . | . | 8·4 | 8·6 | 8·7 | 0·3 |
|  | Base | . | . | . | 2·5 | 3·6 | 4·0 | 1·5 |
| Glycine: Function | Acid | . | . | . | 9·8 | (9·6) | 10·2 | 0·4 |
|  | Base | . | . | . | 2·3 | 3·4 | 3·5 | 1·2 |

TABLE IV.

|  | Water. | 80% EtOH. | 95% MtOH. | MeOH. |
|---|---|---|---|---|
| $-\log K_M$ (solvent)   .   . | 13·9 | 14·8 | 16·1 | 16·7 |

The standard electrode potential of silver-silver chloride (Buckley and Hartley) [7] and the activity coefficients of solutions of hydrogen chloride in methyl alcohol (Nonhebel and Hartley) [4] are known. By making the not unreasonable assumption that the activity coefficients of all the solutions concerned are the same as those of HCl solutions, it is possible to calculate what the potentials of a cell of the type employed should be : the differences between these and the observed potentials give the liquid junction potential. The results (Table V.) show a reasonable constancy. In view of this, a straight line relationship between $p$H and the potential has been assumed.

The accuracy of the dissociation constants determined by this means is probably not greater than $\Delta p_K = \pm 0·1$.
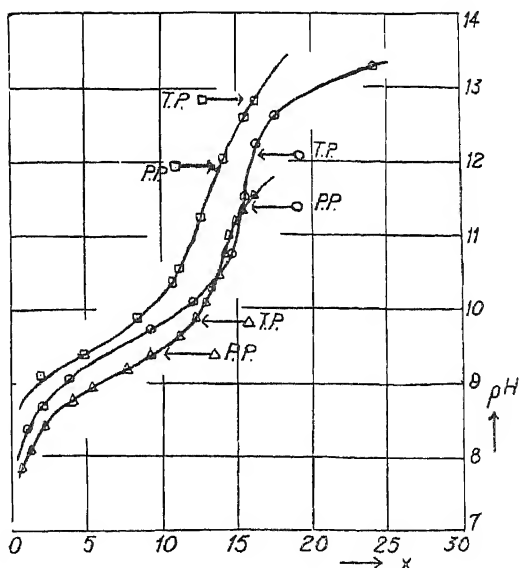


FIG. 3.—Glycine + alkali :
Water △, 80 per cent. EtOH ⊙,
95 per cent. EtOH ⊡.
The turning points of thymol phthalein (T.P.)
and of phenol phthalein (P.P.) are shown by arrows·

[7] Buckley and Hartley, *Phil. Mag.*, 8, 320, 1929.
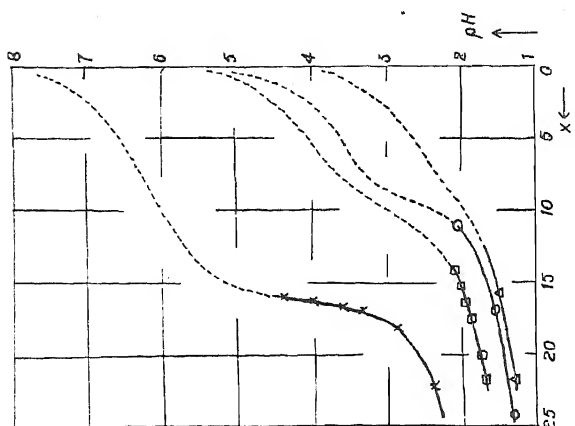
Fig. 6.—" Corrected " curves of tyrosine + acid ; (cf. Fig. 4.)
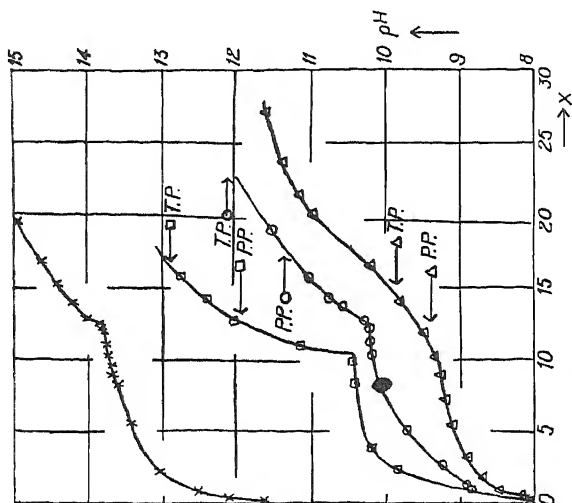
Fig. 5.—Tyrosine + alkali:
Water △,   8o per cent. EtOH ⊙,
95 per cent. EtOH ⊡,   MeOH ×
Turning points of indicators shown by arrows
as in Fig. 3.
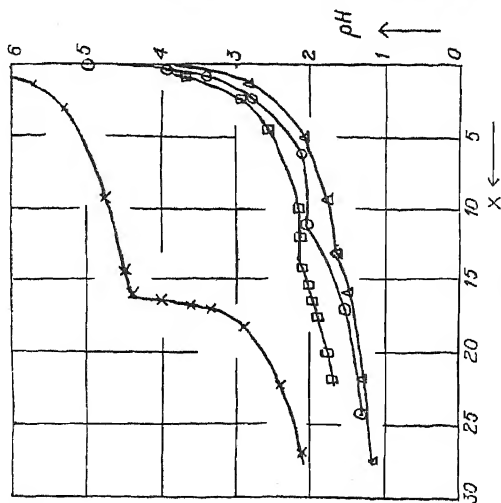
Fig. 4.—Tyrosine + acid :
Water △,   8o per cent. EtOH ⊙,
95 per cent. EtOH ⊡,   MeOH ×.

TABLE V.—LIQUID JUNCTION POTENTIAL IN METHYL ALCOHOL.

| | HCl Solutions. | | | KOMe Solutions. | | |
|---|---|---|---|---|---|---|
| $p_H$ | 1·29 | 1·51 | 1·89 | 14·93 | 15·19 | 15·40 |
| $E_{calc.}$ | 0·146 | 0·157 | 0·180 | 0·924 | 0·938 | 0·950 |
| $E_{obs.}$ | 0·174 | 0·183 | 0·204 | 0·940 | 0·959 | 0·985 |
| $E_{L.J.}$ | 0·028 | 0·026 | 0·024 | 0·016 | 0·021 | 0·035 |

Mean **0·027.**

## Structure of Amino-acids.

The charge type of an acid has an important influence on the change of its constant on passing from one medium to another (Brønsted).[1] The change for a carboxylic acid is of the order of 4·5 $p_K$ units, that for an ammonium acid of the order of 2 $p_K$ units, between water and methyl alcohol ; that this remains true for an amino acid of normal structure is shown by the results for anthranilic acid. The contrast presented by tyrosine is in accordance with its zwitter ion structure ; the levelling effect of the charges carried by the molecule on the changes of the two constants (as compared with anthranilic acid) is in accordance with the predictions of Linderstrøm-Lang.[8] Since the interchange of acid and basic functions within the molecule is a necessary consequence of its zwitter ion structure, it appears that the larger change of constant remains typical of the carboxyl group. The results in mixtures of ethyl alcohol and water show the same effect and are in general agreement with the extensive measurements of Neuberger[9]; the larger change of constant in the basic function identifies the carboxyl group and confirms the zwitter ion nature of glycine and tyrosine.

## Titration of Amino-acids.

For a titration with an indicator to be possible with reasonable accuracy it is necessary that $p_H$ should vary at the end-point with sufficient rapidity and over a sufficient range, and that an indicator should be available, having an observable colour change within the range of the rapid variation of $p_H$ (*cf.* Linderstrøm-Lang).[10] Where the titrand is a base, the lower its $K_A$ value (*i.e.* the greater its strength as a base) and the higher its concentration ; where it is an acid, the less the ratio $K_M/K_A$ (*i.e.* the greater its strength as an acid) or the higher the concentration, the greater will be the rate of variation of $p_H$. This is illustrated by the following equations, obtained by differentiation of (4) and (5) respectively, putting $X = M$ and introducing the approximation $H \gg$ or $\ll$ than $K_M/H$, and $M > K_A > K_M$

$$\text{Basic titrand} \quad \frac{d \ln H}{d \ln X} = \frac{1 + \sqrt{M/K_A}}{2} \qquad . \qquad (10)$$

$$\text{Acidic titrand} \quad \frac{d \ln H}{d \ln X} = \frac{2 + \sqrt{K_A M/K_M}}{4} \qquad . \qquad (11)$$

[8] Linderstrøm-Lang, *Comp. Rend. Lab. Carlsberg*, no. 4, 6, 1927 ; Richardson, *Proc. Roy. Soc.*, 115B, 142, 1934 ; Ogston, *Chem. and Ind.*, 53, 453, 1934.
[9] Neuberger, *Proc. Roy. Soc.*, 115B, 180, 1934.
[10] *Cf.* Linderstrøm-Lang, *Dansk Tidssk. Farmaci.*, 2, 201, 1928.

In the titration of amino acids with strong acid (Linderstrøm-Lang) [11] the effect of adding alcohol is to reduce the value of $K_A$ of the carboxyl group (Figs. 2, 4, 6). In this respect acetone has been found to be more efficient, but the effect is the same. The effect of change of medium on the turning-point of the indicator used (naphthyl red) is very small (Baggesgaard-Rasmussen and Reimers),[12] so that the advantage gained consists entirely in the increase of the rate of change of $p_H$.

In the titration with alkali (Foreman, Willstätter),[13] the change produced in $K_A$ is small, but a considerable decrease of $K_M$ has the same effect as would an increase in $K_A$ (Figs. 3, 5) ; at the same time the dissociation constants of the indicators used (phenol phthalein and thymol phthalein) are much decreased, so that their turning-point falls on the curve near the end point. The advantages of using an alcoholic solvent in these two titrations are illustrated by the curves. It is of interest to note that while pure methyl alcohol is very much better than 95 per cent. ethyl alcohol for the titration with acid, in the titration with alkali the larger decrease of $K_M$ is set off by a comparatively large decrease of $K_A$. This difference is due to the different affinities of the two solvents for protons.

The *Zwitterion* theory has been applied to titrometric methods of determining amino and carboxyl groups in proteolytic work by Linderstrøm-Lang,[8] and his conclusions have been reaffirmed by Richardson,[8] Neuberger [9] and Ogston.[8] Apart from the improvement in the accuracy of titration of *Zwitterions* brought about by a change of medium, the interchange of acid and basic functions due to *Zwitterion* formation necessitates caution in the interpretation of titration data. These can bear their former meaning (namely, that titration with acid estimates amino groups, that with alkali carboxyl groups) only in certain circumstances.

In the following cases errors may arise :—

(1) Where groups other than amino or carboxyl play a part in the *Zwitterion* formation. For example, a compound $^-Y . R . NH_3^+$ will react with one equivalent of alkali irrespective of the nature of Y.

(2) Where the dissociation constants of groups render the standard methods unsuitable for their estimation. For example, $- SO_3^-$ is too weak a base to react completely with acid under normal conditions ; $- NMe_3^+$ will not react at all with alkali ; titration in these cases will give too low values for amino and carboxyl groups respectively. Abnormally weak uncharged carboxylic acids will be incompletely estimated.

(3) Where normal acid groups of sufficient strength other than carboxyl are present (for example, moderately strong phenolic groups) they will react with alkali and appear in the titre as carboxyl.

## Summary.

1. The determination of the dissociation constants of acids from their potentiometric titration curves is discussed.

2. The dissociation constants of ammonia, chloracetic acid, anthranilic acid and tyrosine have been measured in methyl alcohol ; those of

[11] Linderstrøm-Lang, *Z. physiol. Chem.*, **173**, 32, 1928.

[12] Baggesgaard-Rasmussen and Reimers, *Dansk Tidssk. Farmaci*, **225**, 1933.

[13] Foreman, *Biochem. J.*, **14**, 451, 1920 ; Willstätter, *Chem. Ber.*, **54**, 2988, 1921.

tyrosine and glycine in water, 8o per cent. and 95 per cent. ethyl alcohol solutions.

3. The results obtained give support to the zwitter ion hypothesis.

4. The question of estimating amino and carboxyl groups liberated in the process of protein hydrolysis, by the " alcohol " and " acetone " titration methods, is discussed in the light of the zwitter ion hypothesis.

The authors wish to express their thanks to Professor R. A. Peters and to Mr. J. St. L. Philpot for their advice, and to Miss F. J. Ogston for assistance in the earlier stages of this work.

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# SOME ESTIMATED CONSTANTS FOR THE HALOGENS AND THEIR GASEOUS DIATOMIC COMPOUNDS.

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### Introductory Note.

The conception of molecular periodicity proves to be of value in relating together those molecules which are most closely alike from the standpoint of electron configuration, and in permitting estimates to be made of constants in undetermined cases. It is particularly important, as the author has endeavoured to show, to consider molecules in group as well as period arrangement. Up to the present time, application of the method has been somewhat severely restricted to diatomic molecules, for which the term " di-atoms " has been proposed, and some possibly useful relations have been found. The limitation to the simplest case where two atoms only are present is necessitated by sparseness of experimental data concerning the spectroscopic constants of polyatomic molecules. Even in the simplest case, however, examination of the data shows how much remains to be done, in spite of the great output of work in recent years. It seems perhaps appropriate, therefore, in the intervening period whilst further results are awaited, that the available data should be carefully analysed, with a view to the formation of estimates of numbers not yet determined, and to a systemisation of existing knowledge of the field in question. It may be added that some of the numbers derived in the present communication would be very difficult to determine experimentally.

In brief, the method of classification suggested depends, in the cases of non-hydride di-atoms, of distribution into periods depending on the non-bonding electronic groups more or less associated with each nucleus of a di-atom after combination has taken place, and into groups, defined by the number of " shared " electrons derived from the " valency " electrons of the separate atoms, such electrons having their

quantum designations more or less strongly modified after union, as compared with their states in the separated atoms. The Group Number is designated by $n$, and it is found necessary to discuss 13 cases of groups numbered from 2 to 14. The classification is essentially three-dimensional, the details being communicated elsewhere. The periodic groups of hydride di-atoms may be represented in a two-dimensional table similar to the original classification of Mendeljéeff for atoms. The scheme follows lines laid down about two years ago by the author.[1]

In the course of this work, attention became directed to the known failure of Morse's Rule,[2] connecting fundamental vibration frequencies and internuclear distances, to represent the data very accurately. A modified formula has been proposed, in which the square root of the group number of a di-atom and certain "period constants" are introduced. This modification has been found to be reasonably successful in representing the facts concerning the simpler hydride and non-hydride di-atoms, and in enabling predictions to be made of internuclear distances for electronic states in which the fundamental frequency has been determined.[3]

The present paper extends this work to some extent, by suggesting ways in which the principles of classification may be applied to the calculation of certain constants of the halogens and their compounds.

### The Atomic Radius of Fluorine.

A possible check upon calculations made by means of the modified Morse Rule is afforded in the cases of estimates of atomic radii, obtained by halving the internuclear distances of di-atoms where the two component atoms are alike, by comparison of these estimates with results obtained from measurements on crystals.

The predicted value of the equilibrium nuclear separation of fluorine in the lowest state so far [3] analysed ($^1\Pi$) is **1·33** Å.U., giving an estimated atomic radius of $\frac{1}{2} \times 1\cdot331 =$ **0·665** Å.U. The original estimate of W. L. Bragg [4] from crystal data was 0·67 Å.U., whilst a more recent value, due to Neuberger,[5] is 0·68 Å.U. This measure of agreement appears to be sufficiently striking, since in the " KK period " to which the di-atom FF belongs, no experimental data are available for

TABLE I.—ATOMIC RADII OF HALOGEN ATOMS.

| Halogen. | Atomic Radii $r$ (Å.U.). | | | |
|---|---|---|---|---|
| | Calculated (Morse-Clark[3]). | Crystal Data[5]. | Gas[8]. | Band-Spectrum. ($r = \frac{1}{2}r_e$). |
| F . | 0·67 | 0·68 | — | 0·64 (?)[6] |
| Cl . | — | 0·97 | 1·05 | 0·99[8] |
| Br . | — | 1·13 | 1·14 | 1·14[8] |
| I . | — | 1·35 | — | 1·33[8] |

[1] C. H. Douglas Clark, *Chem. Rev.*, **11**, 231, 1932; *ibid.*, Feb. (supplement), 1935.
[2] P. M. Morse, *Physic. Rev.* (ii.) **34**, 57, 1929.
[3] C. H. Douglas Clark, *Phil. Mag.* (vii.), **18**, 459, 1934.
[4] W. L. Bragg, *Phil. Mag.* (vi.), **40**, 169, 1920.
[5] N. V. Sidgwick, *The Convalent Link in Chemistry*, Cornell Univ. Press, 1933. (See p. 85.)

comparison with experiment after the group $n = 12$; a considerable measure of extrapolation is thus involved to the group $n = 14$. So far as the author is aware, no check is yet available from band-spectrum analysis, and the $^1\Pi$ state may not be the ground state, since the other halogens have $^1\Sigma$. Bragg [6] has quoted an internuclear distance obtained from band-spectra of $1\cdot28$ Å.U., which would lead to an atomic radius of $0\cdot64$ Å.U., a value rather lower than those found by other methods. The figure $r_e$ (FF) $= 1\cdot28$ Å.U. applies to the $^1\Pi$ state, and may be subject to alteration, since the quantum numbering of the vibrational levels of this state is still somewhat uncertain: (see note added in proof).

In the cases of the other halogens of group $n = 14$, satisfactory agreement is found between band-spectrum and crystal data for the atomic radii. Hence it appears probable that the present estimate for fluorine lies very near the truth. Table I. shows the results, including in the cases of chlorine and bromine, measurements in the gas phase.

The dotted line (marked HHH) in Fig. I connects together the inter-



FIG. 1.—Internuclear distances of gaseous halides.

nuclear distances of the four halogens. This line, as well as the other lines discussed in the following section, show the " characteristic gradation " (*Abstufung*), or change of slope of property curves noticed by Grimm.[7] The gradation occurs in the dotted line between ClCl and BrBr.
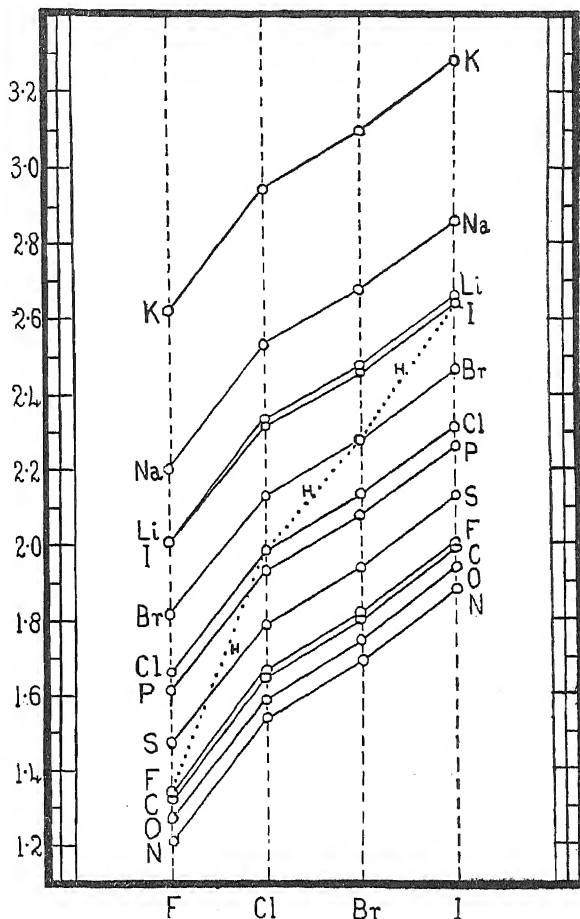
[6] W. L. Bragg, *The Crystalline State*, Vol. I. (G. Bell & Sons, 1933). See Table V. on p. 117.

[7] H. G. Grimm, *Z. Elektrochem.*, **28,** 75, 1922.

## Estimated Internuclear Distances of Gaseous Halides.

It is found that, so far as data are available, the following " Rule of Means " holds fairly accurately : *The internuclear distance of a di-atom* XY *is the arithmetic mean of the internuclear distances of* XX *and* YY. Thus, the following cases of agreement are observed : CN : 1·20 (calc.), 1·17 (obs.) ; NO : 1·15 (calc.), 1·15 (obs.) ; ICl : 2·32 (calc.) 2·31 Å.U. (obs.). A number of other checks are also possible, the maximum error being of the order of ± 0·1 Å.U. It seems, therefore, possible to use the rule in estimation of unknown internuclear distances. The internuclear separations for symmetrical di-atoms are taken from the table due to Jevons,[8] except that of FF, for which the value 1·33 Å.U., calculated from the modified Morse Rule, is used. Proceeding in this way, the estimates given in Table II. are obtained. The numbers placed in brackets are experimental values.

TABLE II.—ESTIMATED INTERNUCLEAR DISTANCES OF HALIDES XY BY THE RULE OF MEANS (Å.U.).

| Y \ X | Li. | Na. | K. | C. | N. | P. | O. | S. | F. | Cl. | Br. | I. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| F | 2·00 | 2·20 | 2·62 | 1·32 | 1·21 | 1·61 | 1·27 | 1·47 | 1·33 | 1·66 | 1·81 | 2·00 |
| Cl | 2·33 | 2·53 | 2·95 | 1·65 | 1·54 | 1·93 | 1·59 | 1·79 | 1·66 | (1·98) | 2·13 | (2·32) |
| Br | 2·48 | 2·68 | 3·10 | 1·80 | 1·69 | 2·08 | 1·74 | 1·94 | 1·81 | 2·13 | (2·28) | 2·47 |
| I | 2·67 | 2·87 | 3·29 | 1·99 | 1·88 | 2·27 | 1·93 | 2·13 | 2·00 | (2·31) | 2·47 | (2·66) |

These numbers are plotted with equal horizontal spacing for the four halogens in Fig. 1. The results show the characteristic gradation mentioned in the preceding section quite clearly.

## The Dipole Moment of Unassociated Hydrogen Fluoride Gas.

Since the hydrogen halides form a natural family of molecules in one periodic group, relations which are found to work fairly accurately for certain cases may with a reasonable measure of certainty be used in other cases. This principle is here applied to the estimation of the dipole moment of HF.

Debye [9] deduced the following relation for the hydrogen halides :—

$$\frac{\mu}{\mu'} = 1 - \frac{\alpha'}{r_e^3} \qquad . \qquad . \qquad . \qquad . \qquad . \quad (1)$$

where $\mu$ is the dipole moment, $\mu'$ is equal to the internuclear distance $r_e$ multiplied by the electronic charge $e = 4·77 \times 10^{-10}$ E.S. units, and $\alpha'$ is the " apparent polarisability " of the negative ion. From this, an " apparent polarisation " $P'$ may be derived by means of a formula of the Debye type :—

$$P' = \frac{4\pi}{3} N\alpha' \qquad . \qquad . \qquad . \qquad . \qquad . \quad (2)$$

where $N$ is the Avogadro Number. Debye showed that the values of $P'$ of HCl and HBr closely approximated to Wasastjerna's estimates of

[8] W. Jevons, *Report on Band-Spectra of Diatomic Molecules* (Cambridge University Press, 1932). See Appendix II. on p. 280.
[9] P. Debye, *Polar Molecules* (Chemical Catalog Co., 1929). See p. 59.

the atomic refractions $R$ of the inert gases argon and krypton respectively, which have the same number of extranuclear electrons.   It was thus found that for HCl, $P' = 4\cdot31$, whilst $R$ (argon) $= 4\cdot23$, and for HBr, $P' = 6\cdot27$, whilst $R$ (krypton) $= 6\cdot42$.   Using the more recent Zahn-van Vleck values of the dipole moments,[10, 11] and more recent values of $r_e$ for the two cases,[8] the numbers shown in Table III. are obtained.   The values of $\mu$ and $\mu'$ are given in Debye units ($10^{-18}$ E.S.U.).

TABLE III.—COMPARISON OF APPARENT POLARISABILITY OF HCl WITH THE MOLECULAR REFRACTION OF ARGON, AND OF THAT OF HBr WITH THE MOLECULAR REFRACTION OF KRYPTON.

| Di-atom. | $r_e \times 10^8$. | $\mu' = r_e e$. | $\mu$. | $\alpha' \times 10^{24}$. | $P'$ (c.c.). | $R$ (Inert Gas). |
|---|---|---|---|---|---|---|
| HCl . . | $1\cdot272$ | $6\cdot067$ | $1\cdot06$ | $1\cdot70$ | $4\cdot32$ | $4\cdot23$ (Ar) |
| HBr . . | $1\cdot411$ | $6\cdot730$ | $0\cdot80$ | $2\cdot48$ | $6\cdot29$ | $6\cdot42$ (Kr) |

Using the principle suggested in the opening paragraph of the present section, the argument may be extended in two ways, to estimate the dipole moment of unassociated HF gas, and to find the equilibrium internuclear distance of HI.

We shall follow Debye's method of calculation, and assume that the apparent polarisability of HF is equal to the molecular refraction of neon, for which Wasastjerna has given the value $R(\mathrm{Ne}) = 1\cdot01$. Taking $P'(\mathrm{HF})$ equal to this, and using the band-spectrum value $r_e(\mathrm{HF})=0\cdot864$ Å.U., we find, by equation (2), that $\alpha'(\mathrm{HF})=0\cdot397\times10^{-24}$. From this, using

$$\mu' = r_e e = 0\cdot864 \times 10^8 \times 4\cdot770 \times 10^{10} = 4\cdot121$$

Debye units, by equation (1), the dipole moment $\mu(\mathrm{HF}) = \mathbf{1\cdot58}$ Debye units, and the dipole distance [12] $t = \mu/e = \mathbf{0\cdot331}$ Å.U.

This estimate fits in with the progression of dipole moments in the series of hydrogen halides, though it may be noted that Smallwood [13] predicts the higher value of $\sim 2\cdot0$ Debye units, by extrapolation.

It is of interest in this connection to observe that the value of $r_e(\mathrm{HF})$ as calculated by the modified Morse Rule, is $0\cdot890$ Å.U., which gives, by the above method, $\mu' = 4\cdot25$, and $\mu = 1\cdot85$ Debye units for HF, the latter figure being closer to Smallwood's estimate.

The calculated dipole moment of HF appears to fit in satisfactorily with that of neighbouring hydides in the periodic classification, as in the scheme herewith.

The relatively high dipole moment of HF in the series of hydrogen halides may be linked with its great capacity to form associated molecules.[14]

| NH$_3$ | OH$_2$ | FH |
|---|---|---|
| $1\cdot48$ | $1\cdot84$ | $1\cdot58$ |
| PH$_2$ | SH$_2$ | ClH |
| $0\cdot55$ | $0\cdot93$ | $1\cdot06$ |
| AsH$_3$ | — | BrH |
| $0\cdot15$ | — | $0\cdot80$ |

[10] C. T. Zahn, *Physic. Rev.* (ii.), **24**, 400, 1924.
[11] J. H. van Vleck, *Physic. Rev.* (ii.), **30**, 31, 1927.
[12] C. H. Douglas Clark, *Physik. Z.*, **35**, 622, 1934.
[13] H. M. Smallwood, *Z. physikal. Chem.*, **B19**, 242, 1932.
[14] J. Simons and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **46**, 2183, 1924.

## The Internuclear Distance of Hydrogen Iodide Gas.

The rule of means as stated above being inapplicable to hydrides, other methods of estimating internuclear distances in these cases must be used.

Using the band-spectrum value [8] $r_0(\text{HI}) = 1\cdot617$ Å.U., and [11] $\mu(\text{HI}) = 0\cdot41\text{D}$, taking $r_0 = r_e$, we find that $\mu'(\text{HI}) = 7\cdot77\text{D}$, and $\alpha'(\text{HI}) = 4\cdot00 \times 10^{-24}$. This gives $P'(\text{HI}) = 10\cdot16$ c.c., which is definitely less than the molecular refraction of xenon $R(\text{Xe}) = 10\cdot56$. The error may be connected with the assumption that $r_0 = r_e$; we may therefore examine what value of $r_e(\text{HI})$ will bring about agreement with Debye's theory.

Taking $P'(\text{HI}) = R(\text{Xe}) = 10\cdot56$, it follows that $\alpha'(\text{HI}) = 10\cdot56/(\frac{4}{3}\pi N) = 10\cdot56/(2\cdot541 \times 10^{24}) = 4\cdot156 \times 10^{-24}$, by equation (2). From this, using equation (1), we have

$$\frac{4\cdot1 \times 10^{-19}}{4\cdot77 \times 10^{-10} \cdot r_e} = \frac{r_e^3 - (4\cdot156 \times 10^{-24})}{r_e^3},$$

or     $8\cdot6 \times 10^{-10} \cdot r_e^2 = r_e^3 - (4\cdot156 \times 10^{-24}).$

This equation may be solved for $r_e$ graphically by forming two equations, by putting $y$ equal to the above left and right hand expressions, and finding the point of intersection of the two lines near to $r_e = 1\cdot6$ Å.U. This yields $r_e(\text{HI}) = \mathbf{1\cdot637}$ Å.U.

It is now possible to prepare a complete table of the dipole moments, dipole distances and equilibrium internuclear separations of the four hydrogen halides (Table IV.). The numbers depending upon estimation are in brackets.

TABLE IV.—DIPOLE MOMENTS AND DISTANCES AND INTERNUCLEAR DISTANCES OF THE HYDROGEN HALIDES.

| Halide. | Dipole Moment $\mu$ Debye Units. | Dipole Distance $l$ Å.U. | Internuclear Distance $r_e$ Å.U. | $\dfrac{100l}{r_e}$ |
|---|---|---|---|---|
| HF . . | (1·58) | (0·331) | 0·864 | (38·3) |
| HCl . . | 1·06 | 0·222 | 1·272 | 17·5 |
| HBr . . | 0·80 | 0·168 | 1·411 | 11·9 |
| HI . . | 0·41 | 0·086 | (1·637) | (5·3) |

With reference to the error inherent in the above calculation, it is found that the calculated values of internuclear distance are not very sensitive to changes in the values of dipole moment; on the other hand, a fairly considerable variation in calculated dipole moment may arise from a relatively small change in internuclear distance. Hence, it is probable that greater weight may be attached to the calculated internuclear distance of hydrogen iodide than to the estimated dipole moment of hydrogen fluoride.

## The Dielectric Constants of the Halogen Gases.

Von Wiśniewski [15] has suggested the following empirical relationship:

$$\sqrt{\epsilon} - 1 = kr_e^3 \qquad . \qquad . \qquad . \qquad . \quad (3)$$

where $\epsilon$ is the dielectric constant of a gaseous di-atom, and $k$ is equal

[15] F. J. v. Wiśniewski, Z. Physik., 44, 392, 1927.

to $3\sqrt{3}\pi N_0 = 3\sqrt{3}\pi \times 2\cdot7 \times 10^{19} = 2\cdot202 \times 10^{20}$, except in the case of hydrogen, where the value of $k$ is three times as great.

In the present section, an attempt is made to test the applicability of the relation to the halogens, in their gaseous ground states.

Some difference of opinion has evidently existed as to whether these molecules have dipole moment or not. Williams and Allgeier [16] have quoted figures for the dipole moments of chlorine ($\mu = 0\cdot13$ D) and of bromine ($\mu = 0\cdot58$ D) obtained by Smyth in calculation. These numbers apparently refer to the liquid states of the two halogens, and, although Zakrewski and Doborzyński [17] have suggested that the polarisations are the same for the gaseous and liquid states, and have given the value $\mu = 0\cdot23$ D for chlorine gas, it is doubtful whether these results can be accepted. According to more recent and very careful measurements of Luft,[18] the dipole moment of bromine vapour is zero to within $0\cdot1$ D. In the following discussion, therefore, we shall take the dipole moments of the halogen gases as zero, and assume the Maxwell relation

$$\epsilon = n_\infty^2 \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

where $n_\infty$ is the refractive index for light of infinite wave-length, to be applicable.

The values of $n_\infty$ for chlorine and bromine are calculated from dispersion formulæ of the Sellmeyer type provided by Cuthbertson and Cuthbertson,[19] giving $n_\infty = 1\cdot000759$ and $\epsilon = \mathbf{1\cdot00152}$ for chlorine, and $n_\infty = 1\cdot001093$ and $\epsilon = \mathbf{1\cdot00218}$ for bromine. In the case of fluorine, according to the measurements of Cuthbertson and Prideaux,[20] the refractive index for the NaD line is $1\cdot000195$ at N.T.P. For the purposes of the present calculation, we shall neglect the difference between this value and $n_\infty$, and take it as an estimate of $\sqrt{\epsilon}$. If now we assume a formula of the Wiśniewski type

$$\sqrt{\epsilon} - 1 = kr_e^x \qquad . \qquad . \qquad . \qquad . \qquad (5)$$

we may attempt to find the value of $x$ best adapted to explain the data, so that $k$ shall be constant. Combining the data for pairs of halogens, we obtain the following values of $x$: $3\cdot41$ (F, Cl), $3\cdot20$ (F, Br), and $2\cdot62$ (Cl, Br). The mean of these numbers is $3\cdot08$, so that $x = 3$ is the nearest whole number to account for the facts, in accordance with v. Wiśniewski's equation (3). If now we use the internuclear distance of fluorine calculated by the modified Morse Rule, and the experimental numbers for chlorine and bromine (Table I.), we find the following values of $k$: $8\cdot27 \times 10^{19}$ (FF), $9\cdot73 \times 10^{19}$ (ClCl), $9\cdot22 \times 10^{19}$ (BrBr). The corresponding value of $k$ for iodine vapour ($\lambda = 0\cdot546\mu$) derived from $n = 1\cdot00216$,[19] is $k = 11\cdot5 \times 10^{19}$, which is rather higher than the mean value for the other halogens ($9\cdot07 \times 10^{19}$). The absolute error, by not using $n_\infty$, increases in the series from fluorine to iodine, however, so the disparity may not be as great as appears at first sight, though the constant is definitely different from the value assigned by v. Wiśniewski ($22\cdot02 \times 10^{19}$). On the whole, though there appears to be a slight tendency for $k$ to increase in the series from FF to II, a suitable average value to take for the group would appear to be about $\mathbf{9\cdot5 \times 10^{19}}$.

[16] J. W. Williams and R. J. Allgeier, *J. Amer. Chem. Soc.*, **49,** 2916, 1927.
[17] C. Zakrewski and D. Doborzyński, *Bull. Acad. Polonaise*, **6a,** 300, 1930.
[18] K. F. Luft, *Z. Physik*, **84,** 767, 1933.
[19] C. Cuthbertson and Maude Cuthbertson, *Phil. Trans.*, **A213,** 1, 1913.
[20] C. Cuthbertson and E. B. R. Prideaux, *Phil. Trans.*, **A205,** 319, 1906

Applying this to the cases where $n_\infty$ has not been determined, and using equation (4), we find that $n_\infty = 1 \cdot 00022$ and $\epsilon = 1 \cdot 00045$ for fluorine, and $n_\infty = \mathbf{1 \cdot 00179}$ and $\epsilon = \mathbf{1 \cdot 00357}$ for iodine, at N.T.P. It should be noted that the estimated $n_\infty$ (FF) is greater than the experimental value for the NaD line, so that this estimate is probably too high.

It becomes possible to form an independent estimate of the above values by means of the atom refractions of the halogens $R_A$ deduced from the study of the contributions made to molecular refractions in organic compounds : F $= 1 \cdot 09$ ; Cl $= 5 \cdot 96$ ; Br $= 8 \cdot 86$ ; I $= 13 \cdot 90$ (NaD line at 20° C.). We may then write

$$\frac{n_\infty^2 - 1}{3} \cdot \frac{M}{d} = \frac{\epsilon - 1}{3} \cdot \frac{M}{d} = 2R_A,$$

or $\quad n_\infty^2 - 1 = \epsilon - 1 = 6R_A/22{,}410 = R_A/3{,}735 = 0 \cdot 0002677 R_A \quad$ (6)

very approximately. For the purposes of this calculation, the differences between $n_\infty$ and $n$ (NaD, 20° C.) are neglected, the results being shown in Table V. The numbers shown in heavy type are the chosen estimates.

TABLE V.—DIELECTRIC CONSTANTS AND REFRACTIVE INDICES OF THE HALOGENS.

| Halogen Di-atom. | Dielectric Constant $\epsilon$. | | | Refractive Index $n_\infty$. | | |
|---|---|---|---|---|---|---|
| | N.T.P. (Expt. ([19])). | N.T.P. Calc. Eq. (3). | NaD 20° C. Calc. Eq. (6). | N.T.P. (Expt. ([19])). | N.T.P. Calc. Eqs. (3)(4). | NaD 20° C Calc. Eq. (6). |
| FF  . | — | 1·00045 | 1·00030 | — | 1·00022 | 1·00015 |
| ClCl  . | 1.00152 | — | 1·00160 | 1.00076 | — | 1·00080 |
| BrBr  . | 1.00218 | — | 1·00237 | 1.00109 | — | 1·00119 |
| II | — | **1.00357** | 1·00372 | — | **1.00179** | 1·00186 |

Judging by the measure of applicability found for v. Wiśniewski's Rule, and the experimentally determined index of refraction for fluorine, ($1 \cdot 000195$ NaD), the figures deduced by equation (6) are unreliable in this case. The electron configuration of fluorine ($z\sigma^2 y\sigma^2 x\sigma^2 w\pi^4 v\pi^4$) is complex, and involves fourteen shared electrons. The $y$ and $v$ groups are supposed, in Mulliken's theory, to be anti-bonding, and to neutralise an equal number of bonding electrons in each case, leaving two electrons over to form a single bond. This may not be completely true, and may affect the additivity of refraction of the atoms. The nuclear charges being increasingly greater from FF to II, it appears that the bond linking the two atoms together becomes increasingly like a similar single bond in an organic compound. This explanation seems at any rate consistent with the facts. A similar break-down of the simple additivity rule appears in the hydrogen halides (see next section). Since $n_\infty$ (FF) appears to lie between the upper and lower limits shown in Table V., an approximation may be made taking the mean : $n_\infty$ (FF) $= \mathbf{1 \cdot 00019}$. This gives $\epsilon$ (FF) $= \mathbf{1 \cdot 00038}$.

Atom polarisation is neglected in making these estimates, but it is probably small.

The value of v. Wiśniewski's constant, in the case of hydrogen, is found to be $32 \cdot 65 \times 10^{19}$, which is not far from three and a half times

as great as the chosen value for the halogens ($335 \times 9.5 \times 10^{19} = 33.25 \times 10^{19}$). v. Wiśniewski predicted the value $3 \times 22.02 \times 10^{19} = 66.06 \times 10^{19}$.

## The Dielectric Constants of the Gaseous Hydrogen Halides.

Von Wiśniewski [21] attempted to apply his equation (3) to HCl and HBr, using equation (4) to deduce $\epsilon$ from refractive index. This procedure completely fails in two ways : first, because the Maxwell relation cannot be applied to cases where orientation polarisation is present, and, secondly, because the dielectric constants under the same conditions decrease, whilst the nuclear separations increase, in the series $HCl \rightarrow HBr \rightarrow HI$. Hence neither equation (3) nor (4) is applicable to the hydrogen halides, and any calculations based upon these premises are invalidated.

It is evidently necessary to apply formulæ of the well-known type suggested by Debye (equations (7) and (8) below) :—

$$\frac{\epsilon - 1}{3} \cdot \frac{M}{d} = \frac{n_\infty^2 - 1}{3} \cdot \frac{M}{d} + \frac{4}{3}\pi N \frac{\mu^2}{3kT} \qquad . \qquad . \quad (7)$$

$$\frac{\epsilon - 1}{3} \cdot \frac{M}{d} = \frac{4}{3}\pi N \left( \alpha + \frac{\mu^2}{3kT} \right) \qquad . \qquad . \qquad . \quad (8)$$

where $\epsilon$ is the dielectric constant of a gas at N.T.P., $M/d$ is the grammolecular volume (22,410 c.c.), $N$ is the Avogadro Number ($6.064 \times 10^{23}$), and $k$ is Boltzmann's constant ($1.371 \times 10^{-16}$ erg per degree per molecule).[22]

For the purpose of the calculation, Born and Heisenberg's $\alpha$'s [23] for the negative ions are used in the first instance, with a suitable correction afterwards introduced as explained below. If we insert values of $n_\infty$ derived from the equations of Cuthbertson and Cuthbertson [19] into equation (7) for the halide gases (except HF), independent estimates of $\epsilon$ are obtained. Further, we may compare these estimates, again with the exception of HF, with the experimental values of Zahn [10] suitably interpolated for 273° K, using corrected values of $\alpha$. Finally, we obtain estimates of $n_\infty$ on the assumption of additivity of atom refraction, taking $R_A$ (hydrogen) $= 1.10$. This gives the values of $R_M$: HF 2.19 ; HCl 7.06 ; HBr 9.96 ; HI 15.00. The relation connecting $n_\infty$, $\alpha$ and $R_M$ will be :—

$$\frac{n_\infty^2 - 1}{3} \cdot \frac{M}{d} = \frac{4}{3}\pi N \alpha = R_M \qquad . \qquad . \qquad . \quad (9)$$

whence $\qquad n_\infty^2 - 1 = 3R_M/22,410 = 0.0001339 R_M \qquad . \qquad . \quad (10)$

and $\qquad n_\infty^2 - 1 = 3.402 \times 10^{20} \alpha \qquad . \qquad . \qquad . \quad (11)$

These relations give the results shown in Table VI., as explained on following page.

It will be noted that, according to equation (9), $\alpha$ should be proportional to $R_M$. Since this does not hold for the additivity numbers in the column $R_M$ and Born and Heisenberg's $\alpha$'s for the negative ions, some adjustment of these numbers is necessary.

[21] F. J. v. Wiśniewski, *Z. Physik*, **37**, 126, 1926.
[22] C. H. Douglas Clark, *Phil. Mag.* (vii.), **18**, 80, 1934.
[23] M. Born and W. Heisenberg, *Z. Physik*, **23**, 388, 1924.

TABLE VI.—Dielectric Constants and Refractive Indices of the Hydrogen Halides at N.T.P.

| Halide Di-atom. | $\mu$ (D). | Refractive Index $n_\infty - 1 (\times 10^6)$. | | | $\alpha$ $(\times 10^{24})$ | $\alpha''$ $(\times 10^{24})$ | $R_M$. | $R''_M$. | Dielectric Constant $\varepsilon - 1 (\times 10^5)$. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | expt.[19] | Calc. | | | | | | Calc. eq. (8). | | Expt. Zahn[10] |
| | | | eq. (10). | eq. (11). | | | | | $\alpha_\infty$ | $\alpha''$. | |
| HF . | (1·58) | — | 128 | 168 | 0·99 | 0·80 | 2·19 | 2·03 | — | 783 | — |
| HCl . | 1·06 | 435 | 473 | 518 | 3·05 | 2·56 | 7·06 | 6·49 | 444 | 427 | 430 |
| HBr . | 0·80 | 594 | 667 | 709 | 4·17 | 3·49 | 9·96 | 8·87 | 336 | 313 | 315 |
| HI . | 0·40 | 883 | 1004 | 1068 | 6·28 | 5·18 | 15·00 | 13·18 | 264 | 228 | 234 |

The calculated refractive indices using equation (10) differ very considerably from the experimental values ; this is in accordance with anticipation, since additivity of molecular refraction cannot, in general, be expected to hold in the case of " united-atoms." The additivity relation is much more nearly correct for the halogens, except for FF, as noticed in the preceding section. If now we calculate what values of $R_M$, which we may call $R''_M$, will give the experimental values of $n_\infty^2 - 1$ for HCl, HBr and HI, the numbers given in the appropriate column are found. The difference $R''_M - R_M$ increases from HCl to HI, with increasing deformability of the halogen atom.

The deviations from the requirements of additivity of molecular refraction increase in the series from HF to HI and in the series from II to FF, this conclusion, however, being less certain for the latter series.

The calculated refractive indices using equation (11) differ still more widely from the experimental values ; this may doubtless be associated with the fact that Born and Heisenberg's $\alpha$'s were derived from measurements of Spangenberg on solid salts, and that therefore these numbers cannot be applied without modification to the gaseous di-atoms. However, there is an almost constant percentage error in these numbers : the values of $n_\infty^2 - 1$ are about 19·1, 19·4 and 20·9 per cent. higher than the corresponding experimental numbers for gaseous HCl, HBr and HI respectively. It appears that we may reduce the refractive index found for HF by using equation (11) by 19 per cent., in order to obtain an estimated value. This gives $n_\infty$ (HF) $= 1.000136$, which is not very different from the value obtained by the use of equation (10). This indicates that additivity of molecular refraction holds best for HF in the series of hydrogen halides, as would be expected, since the fluorine atom is the smallest and least deformable. The value of $R''_M$(HF), using equation (10), is 2·03, whilst the additivity value is $R_M$ (HF) $= 2·19$.

It might be argued that a smaller diminution than 19 per cent. should be used in estimating $n_\infty$ (HF), since the positive errors decrease somewhat using equation (11) from HI to HCl. This, however, would yield a larger value of $R''_M$, which can hardly be greater than $R_M$. Hence it would appear that approximately the right correction has been made.

We next proceed to find what value of $\alpha$, which we may designate by $\alpha''$, will fit the experimental values of $n_\infty - 1$ for HCl, HBr and HI, and the estimated value for HF, using equation (11). In this way, the values shown in the appropriate column of Table VI. are obtained.

A rough calculation shows that the dielectric constants of HCl, HBr and HI calculated by equation (7) from the experimental values of $n_\infty$ agree satisfactorily with the experimental values of Zahn. On the other hand, as Table VI. shows, the use of Born and Heisenberg's $\alpha$'s in equation (8) gives too high values of $\epsilon$ for these cases. This clearly suggests that $\alpha''$ rather than $\alpha$ should be used in equation (8), leading to the numbers shown in the last column but one of Table VI. The very satisfactory agreement suggests that the method of calculation is sound. It is observed that the calculated values lag slightly behind the experimental, which seems to be due to the neglect of atom polarisation. The general opinion of various authorities,[24] however, is that the atom polarisation is negligibly small.

Since the percentage errors tend to diminish from HI to HCl in the last two columns of Table VI., it appears that the error should be small in forming the estimate $\epsilon(HF) = \mathbf{1 \cdot 00783}$. This value, however, depends upon the earlier estimate of $\mu(HF)$, which it is hoped may prove itself trustworthy. An experimental check, in these cases, however, would unfortunately be very difficult to carry out.

The results for the halogens and their hydrides may be tabulated as opposite, those obtained in the present communication being distinguished by heavy type.

Whilst no definite limits of accuracy, in general, have been assigned to the estimated numbers, attention has been paid to their relative weight in the text of the communication.

| Di-atom. | $r_e$ (A.U.). | $\mu$(D). | $\epsilon$(N.T.P.). | $n_\infty$. |
|---|---|---|---|---|
| FF | 1·33 | 0 | 1·00038 | 1·00019 |
| ClCl | 1·983 | 0 | 1·00152 | 1·00076 |
| BrBr | 2·28 | 0 | 1·00218 | 1·00109 |
| II | 2·66 | 0 | 1·00357 | 1·00179 |
| HF | 0·864 | 1·58 | 1·00783 | 1·000136 |
| HCl | 1·272 | 1·06 | 1·00430 | 1·000435 |
| HBr | 1·411 | 0·80 | 1·00315 | 1·000594 |
| HI | 1·637 | 0·41 | 1·00234 | 1·000883 |

The author desires to express his thanks to Dr. F. R. Goss for kindly interest and criticism during the preparation of this paper.

*Note added in Proof.*—The atomic radius of fluorine given in the above text was calculated from $\omega_e(FF) = 1081 \cdot 4$ cm.$^{-1}$ for the $^1\Pi$ state given by Jevons.[8] Dr. Jevons, in a private communication to the author, states that this value was based upon measurements and assignments of vibrational quantum numbers made by Gale and Monk in 1927. Further measurements by these authors in 1929 yielded a more probable, though still uncertain, value of $\omega_e = 1139 \cdot 8$ cm.$^{-1}$ This gives $r_e(FF) = 1 \cdot 30$ Å.U. by an application of the modified Morse Rule, as against the experimental figure $r_e = 1 \cdot 278$ Å.U. This latter is doubtless the value quoted by Bragg,[6] but it is uncertain, since the $v''$ numbering is, as Gale and Monk admit, not definitely ascertained. Moreover, even if the $v''$ numeration is correct, and the spectroscopic numbers $1139 \cdot 8$ and $1 \cdot 278$ do therefore actually refer to $\omega_e$ and $r_e$ respectively, $^1\Pi$ state is probably not the ground state. Since, however, Table I. of the above communication shows close agreement between spectroscopic and crystal data for the other three halogens, it seems not unreasonable to suppose that the

[24] J. H. van Vleck, " Electric and Magnetic Susceptibilities " (Oxford University Press, 1932, p. 52) ; C. P. Smyth, *J. Amer. Chem. Soc.*, **51**, 2051, 1929 ; *J. Chem. Physics*, **1**, 247, 1933 ; F. Fairbrother, *Trans. Faraday Soc.*, **30**, 862, 1934.

value of $\omega_e(\mathrm{FF}) \approx 1080$ cm.$^{-1}$ in the ground state. This might indeed be regarded as an approximate estimate of this number, for which no data from band spectra are at present available. Regarded in this light, the results based upon the present estimate of $r_e(\mathrm{FF}) = 1\cdot33$ A.U. may still be presumed to be reasonably trustworthy.

With reference to the estimate of the dipole moment of HF, Kirkwood [25] has calculated the value $1\cdot30$, in agreement with the author's value, considering the limits of error of Kirkwood's method. On the other hand, Kirkwood finds $\mu(\mathrm{HF})$ to be smaller than $\mu(\mathrm{HCl})$, and holds that the polarisabilities of the fluorine ion and neon are unequal, though the values for the other halogens and their corresponding inert gases are about the same. Smith and McAlpine,[26] using Kirkwood's data, find the lower value $\mu(\mathrm{HF}) = 0\cdot80$ D, whilst Malone [27] adopts an estimate on the higher side of $2\cdot00$ D, in agreement with the estimate of Smallwood.[13]

It may finally be added that Wassiliew and collaborators [28] find the dipole moment of iodine dissolved in benzene and carbon disulphide to be zero, in agreement with the assumption made by the present author for the gas phase.

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*University of Leeds,* 2.

[25] J. G. Kirkwood, *Physik. Z.*, **33**, 259, 1932.
[26] C. P. Symth and K. B. McAlpine, *J. Chem. Physics*, **2**, 499, 1934.
[27] J. G. Malone, *J. Chem. Physics*, **1**, 197, 1933.
[28] W. Wassiliew, J. Syrkin, and I. Kenez, *Nature*, **135**, 71, 1935.

# THE HEATS OF REACTION AND VISCOSITIES OF ETHER CHLOROFORM MIXTURE.

By D. B. MACLEOD, M.A., D.Sc. AND F. J. WILSON, B.Sc.

The problem of the nature of molecular association in pure liquids and of compound forming in liquid mixtures is still largely unsolved. The type of binding in these compounds is that due to the ill-defined stray valencies of the molecule. The compounds formed, therefore, have little stability. Nevertheless such marked and definite changes take place on mixing various pairs of liquids, that some form of combination seems certain. Very considerable amounts of heat are evolved and the physical properties of the mixture showed a marked divergence from the mean of the constituents. In many cases definite compounds have been separated by freezing.

The subject has recently been discussed by Macleod.[1] An expression proposed for the viscosities of binary mixtures took the form

$$\eta = \left[ \eta_1 m_1 \frac{x_1}{x} + \eta_2 m_2 \frac{x_2}{x} \right] \frac{M_a}{M_c}$$

[1] *Trans. Faraday Soc.*, 1934, **30**, 482.

where $\eta_1$ and $\eta_2$ are the viscosities of the pure constituents, $m_1$ and $m_2$ their molecular percentages, $x_1$ and $x_2$ their amounts of free space per c.c. and $x$ the free space of the mixture. $M_c$ is the mean molecular weight of the constituents before mixing and $M_a$ the actual mean molecular weight after mixing. This expression was applied to a number of mixtures studied by Bramley.[2]

In order to provide fresh material with which to check the value of the above expression, measurements of the heats of reaction of ether-chloroform mixtures were undertaken by one of us.

Ether and chloroform are more suitable liquids to study than those chosen by Bramley [2] because they both belong to the class of normal or unassociated liquids. It is somewhat of a disadvantage that ether is rather near its boiling-point at ordinary temperatures, which limits the range of temperature over which experiments can be made, without facing the difficult problems of technique at low temperatures.

## Measurement of the Heat of Reaction.

1. A silvered Dewar flask (Fig. 1) of capacity 400 c.c., containing a weighed quantity of distilled water, approximately 200 grams, acted as the calorimeter.

2. The reaction chamber R, made of thin copper, and of 40 c.c. capacity, contained a weighed quantity of ether. This was suspended in the water by an insulating glass rod D and contained a small stirrer worked by a thread through the lid. A small hole in the lid also enabled the tip of a pipette, bent as shown in the figure, to pass into it. The pipette contained a weighed quantity of chloroform. A Beckmann Thermometer, a Standardised Thermometer reading to $1/10°$ C. and a stirrer were also in the water in the calorimeter.

3. After allowing sufficient time for the whole of the apparatus to assume the temperature of the water in the calorimeter, the chloroform was blown into the reaction vessel and the pipette reweighed.



FIG. 1.

The mixture of the two constituents in the reaction tube were thoroughly stirred and also the water of the calorimeter. After a definite interval, namely, four minutes, the Beckmann Thermometer reached a steady state and the reading on it and the Standard Thermometer were noted. A maximum rise of temperature of about $1°$ C. was obtained. The Beckmann was graduated to $1/100°$ C. and with the aid of a reading microscope readings to the next place of decimal could be taken with fair accuracy.

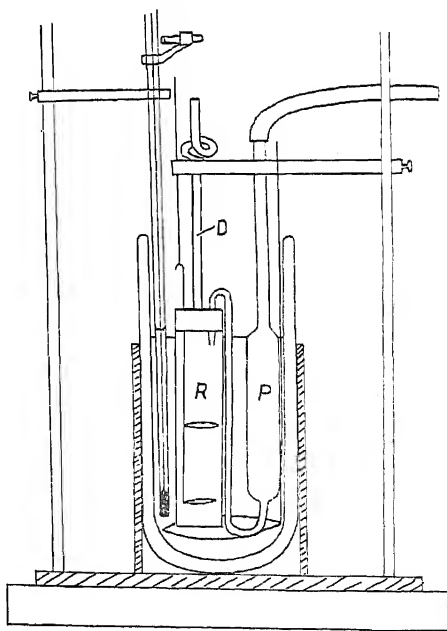The combined weight of the ether and chloroform was about 30 grams.

[2] *J.C.S.*, 1916, **109**, 11-45 and 343-519.

## Corrections.

1. The water equivalent of the calorimeter and its contents was determined experimentally. The mean of a number of values was 18·0 Cals.

2. On account of the large volume of water compared with the volume of the reacting substances, the correction for the true specific heat of the mixtures as distinct from that of the mean of the constituents, became relatively small. Values of the specific heat of ether-chloroform mixtures are, however, quoted by Dolazalek and Schulze,[3] as shown in Table I.

TABLE I.—SPECIFIC HEAT OF ETHER-CHLOROFORM MIXTURES.

| Mol. Per Cent. Chloroform. | 50° C. | 0° C. | 20° C. |
|---|---|---|---|
| 0·0 | 0·467 | 0·521 | 0·539 |
| 0·2 | 0·573 | 0·514 | 0·482 |
| 0·4 | 0·594 | 0·482 | 0·431 |
| 0·5 | 0·570 | 0·453 | 0·401 |
| 0·6 | 0·530 | 0·419 | 0·367 |
| 0·8 | 0·399 | 0·329 | 0·298 |
| 1·00 | 0·226 | 0·232 | 0·234 |

The specific heats of the mixtures used in these experiments were obtained from these figures by interpolation graphically.

3. Determinations of the loss or gain of heat by the calorimeter during the experiments made above and below room temperatures, were obtained by observing the average change of temperature over a period of four minutes—the period of the experiment—immediately preceding the mixing of the liquids. The correction was found to be + ·022° C. at 25° C. and − ·031° C. at 3° C.

## Purification of the Constituents.

Ether.—Commercial ether, 0·720 density, was purified by leaving about 1 litre over caustic soda sticks for one day, washed with concentrated caustic soda solution, left over caustic soda sticks again, and finally dried over anhydrous calcium chloride. The calcium chloride was filtered off, distilled, and sodium wire passed into the purified ether which was contained in a well-stoppered dark glass bottle.

Small quantities were distilled at intervals and only the constant boiling fraction at 35·6° C. was taken for use in the experiments.

Chloroform. — Commercially pure chloroform was treated with caustic soda sticks for one day, washed twice with concentrated sulphuric acid, once with distilled water, then with dilute caustic soda solution and lastly with distilled water. It was dried with anhydrous calcium chloride and finally with phosphoric oxide. It was distilled over phosphoric oxide and the portion distilling at constant boiling-point 62° C. was taken and kept in a dark blue bottle. The frac-
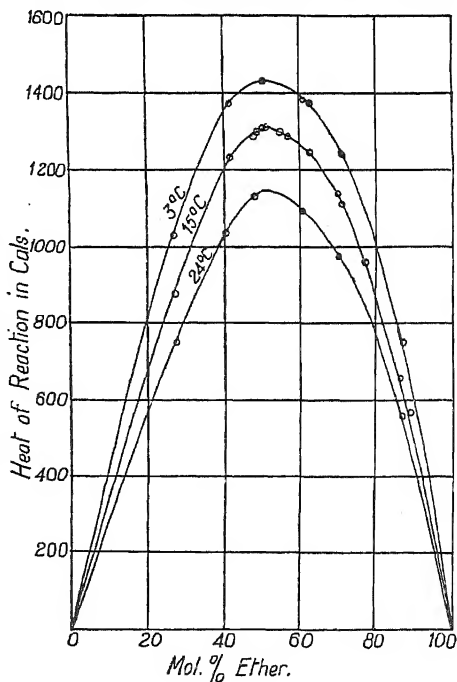


FIG. 2.

[3] Z. physik, Chem., 1913. 83.

tions used in working were distilled at frequent intervals over phosphoric oxide.   The purities of both constituents were verified by their densities.

Measurements of the heats of reaction were made at 3° C., 15° C., and 24° C.   Small divergences from these final temperatures were corrected for graphically.

The experimental values obtained are shown in Table II.

These results are shown graphically in Fig. 2 where the heats of reaction are plotted against the molecular percentages.

## Discussion of Results.

It is evident that the maximum occurs at or very close to equimolecular proportions.   This would indicate that any compound forming was of the nature of one molecule of ether with one of chloroform.   The law of mass action for a reaction of this type, namely,

$$K = \frac{(a - x)(b - x)}{Vx}$$

where $a$ and $b$ are the initial number of gram molecules of the pure constituents and $x$ the gram molecules of the combined molecules in a volume $V$, can be rewritten,[2]

$$K = \frac{(a - cH)(b - cH)}{VcH}$$

on the assumption that the number of gram molecules of the compound is proportional to the heat of reaction, $H$. There are here two unknown constants, $c$ and $K$, which can be solved by taking a typical pair of experimental results.   In order to apply this expression it is necessary to know the densities of the mixtures.   An experimental determination of the mean coefficients of expansion from 0° to 18° C. of the following mixtures gave the results in Table III.

These coefficients of expansion were taken in conjunction with the densities at 0° C. of mixtures of ether and chloroform determined by Thorpe and Rodger.[4]

The densities of the various mixtures were obtained from these tables graphically.

Table V. shows the application of the law of mass action to the heats of reaction at 15° C.   The heats of reaction have been calculated for 100 c.c. of each mixture, so that $V$ is eliminated.   The columns $a$ and $b$ give the number of gram molecules of ether and chloroform, respectively, in 100 c.c. of each mixture.   Unfortunately, because of the

TABLE II.

| Wt. Per Cent. Ether. | Mol. Per Cent. Ether. | Cals. per 193·46 grs. (Gram Molecule). |
|---|---|---|
| **Temperature, 15° C.** | | |
| 83·60 | 89·10 | 562·0 |
| 80·24 | 86·74 | 654·8 |
| 67·75 | 77·16 | 958·7 |
| 61·24 | 71·80 | 1107·0 |
| 59·77 | 70·54 | 1136·3 |
| 51·02 | 62·66 | 1241·6 |
| 44·66 | 56·53 | 1286·3 |
| 43·05 | 54·90 | 1291·3 |
| 39·57 | 51·35 | 1308·4 |
| 38·90 | 50·62 | 1303·2 |
| 37·86 | 49·53 | 1294·3 |
| 36·63 | 48·23 | 1289·1 |
| 30·65 | 41·59 | 1219·6 |
| 18·54 | 26·83 | 866·4 |
| **Temperature, 3° C.** | | |
| 80·55 | 86·99 | 747·1 |
| 60·15 | 70·86 | 1239·8 |
| 51·00 | 62·65 | 1377·1 |
| 49·88 | 61·59 | 1381·3 |
| 38·86 | 50·59 | 1439·3 |
| 38·74 | 50·46 | 1435·3 |
| 30·56 | 41·49 | 1363·6 |
| 18·93 | 27·34 | 1028·2 |
| **Temperature, 24° C.** | | |
| 80·14 | 86·68 | 558·0 |
| 59·20 | 70·04 | 973·6 |
| 49·13 | 60·88 | 1098·6 |
| 37·14 | 48·77 | 1138·7 |
| 29·46 | 40·22 | 1028·8 |
| 18·88 | 27·28 | 743·1 |

mathematical form of the mass action law, considerable variations can be made in the values of $c$ and $H$ without having a marked effect on the constancy of $K$. This renders this method of estimating the percentage of combined molecules somewhat uncritical. In the following table, two values of $c$, viz. $c_1$ and $c_2$ are chosen over the range where the corresponding values of $K$, namely $K_1$ and $K_2$ are almost constant.

The constancy of $K$ leaves little doubt that the reaction is essentially the combination of one molecule of ether with one of chloroform to form a compound molecule. The value 0·000100 for $c$, corresponds to 14 per cent. of the molecules being combined at equimolecular proportions, while the value 0·000153 corresponds to 20

TABLE III.

| Wt. Per Cent. Ether. | Mean Coeff. of Expansion for 1° C. |
|---|---|
| 0 | 0·001260 |
| 19·20 | 0·001302 |
| 38·33 | 0·001358 |
| 69·23 | 0·001453 |
| 100·00 | 0·001582 |

TABLE IV.

| Wt. Per Cent. Ether. | Density. |
|---|---|
| 0 | 1·5255 |
| 15·94 | 1·3136 |
| 40·14 | 1·0801 |
| 59·80 | 0·9389 |
| 79·30 | 0·8292 |
| 100·00 | 0·7362 |

per cent. At 30 per cent. the constancy of $K$ becomes less satisfactory. The method, therefore, while indicating the nature of the reaction, does not give the number of combined molecules with any precision. A value from 14 to 20 per cent. at 15° C. would, however, be indicated.

A preliminary discussion of the ether-chloroform mixture at 0° C.

TABLE V.

Temp. 15° C.   $c_1 = 0·000100$ ; $c_2 = 0·000153$.

| Wt. Per Cent. Ether. | Density. | a. | b. | Heat for 100 c.c. Mixture. | $K_1$. | $K_2$. |
|---|---|---|---|---|---|---|
| 100·00 | — | — | — | — | — | — |
| 83·60 | 0·7870 | 0·8883 | 0·1081 | 228·5 | 0·0324 | 0·0178 |
| 80·24 | 0·8046 | 0·8717 | 0·1332 | 272·2 | 0·0328 | 0·0181 |
| 69·75 | 0·8707 | 0·7962 | 0·2352 | 431·3 | 0·0335 | 0·0187 |
| 61·24 | 0·9109 | 0·7530 | 0·2957 | 521·0 | 0·0327 | 0·0182 |
| 59·77 | 0·9210 | 0·7432 | 0·3103 | 541·0 | 0·0326 | 0·0181 |
| 51·02 | 0·9795 | 0·6746 | 0·4019 | 628·5 | 0·0330 | 0·0183 |
| 44·66 | 1·0243 | 0·6174 | 0·4747 | 680·8 | 0·0328 | 0·0182 |
| 43·05 | 1·0387 | 0·6036 | 0·4953 | 693·3 | 0·0328 | 0·0182 |
| 39·57 | 1·0673 | 0·5701 | 0·5401 | 721·1 | 0·0323 | 0·0179 |
| 38·90 | 1·0701 | 0·5618 | 0·5475 | 720·5 | 0·0323 | 0·0179 |
| 37·86 | 1·0798 | 0·5518 | 0·5620 | 722·0 | 0·0325 | 0·0180 |
| 36·63 | 1·0888 | 0·5384 | 0·5778 | 725·5 | 0·0324 | 0·0179 |
| 30·65 | 1·1389 | 0·4712 | 0·6615 | 718·3 | 0·0328 | 0·0181 |
| 18·54 | 1·2641 | 0·3163 | 0·8623 | 566·0 | 0·0370 | 0·0205 |
| 0·00 | — | — | — | — | — | — |

was given by Macleod in the earlier paper.[1] A further analysis will now be given following the method of the above paper. Thorpe and Rodger,[4] though they supply the densities of the other mixtures studied by them, in the case of ether and chloroform, only give the densities at 0° C. They remark that " where the difference between the coefficients of thermal expansion of the constituents is small, the coefficients of

the mixtures may be calculated with sufficient accuracy by the ad-
mixture rule and it was, therefore, deemed unnecessary for so small
a range of temperature to make observations on the thermal expansion
of the mixtures."

An experimental determination of the coefficients of expansion
of ether-chloroform mixtures, quoted earlier in the paper, revealed a
departure from the mixture law, the mixtures having a slightly lower
coefficient of expansion than that calculated from the pure constituents.

Unfortunately, an error crept into the figures given in the original

TABLE VI.

| Wt. Per Cent. Ether. | Mol. Per Cent. Ether. | Contr. for I c.c. | $x_o.$ | $x_c.$ | $\eta_o.$ | $\eta_c.$ | $M_a/M_c.$ |
|---|---|---|---|---|---|---|---|
| **Temperature, 0° C.** | | | | | | | |
| 0 | — | — | 0·1055 | — | 0·00700 | — | — |
| 15·94 | 23·40 | 0·0082 | 0·1152 | 0·1070 | 0·00678 | 0·00617 | 1·10 |
| 40·14 | 51·92 | 0·0126 | 0·1256 | 0·1130 | 0·00562 | 0·00498 | 1·13 |
| 59·80 | 70·55 | 0·0098 | 0·1315 | 0·1217 | 0·00440 | 0·00410 | 1·07 |
| 79·30 | 86·04 | 0·0049 | 0·1362 | 0·1312 | 0·00350 | 0·00340 | 1·03 |
| 100·00 | — | — | 0·1400 | — | 0·00286 | — | — |
| **Temperature, 10° C.** | | | | | | | |
| 0 | — | — | 0·1180 | — | 0·00626 | — | — |
| 40·14 | 51·92 | 0·0132 | 0·1397 | 0·1265 | 0·00489 | 0·00445 | 1·10 |
| 100·00 | — | — | 0·1552 | — | 0·002585 | — | — |
| **Temperature, 20° C.** | | | | | | | |
| 0 | — | — | 0·1309 | — | 0·00564 | — | — |
| 40·14 | 51·92 | 0·0136 | 0·1544 | 0·1408 | 0·00430 | 0·00400 | 1·075 |
| 100·00 | — | — | 0·1712 | — | 0·002345 | — | — |

paper. The column given as the molecular percentage of ether should
have been the volume percentage. Though the molecular percentages
were actually used in the calculation of the result, a slight error also
occurred in these figures, the weight percentage of 40·14 per cent. ether
having been taken as equivalent to a molecular percentage of 50·30
instead of 51·92. The corrected table at 0° C. and the values at 10° C.
and 20° C. for the 51·92 per cent. molecular mixtures are given in Table VI.
As in the earlier paper, the column $x_o$ gives the free space without allow-
ance for the contraction on mixing, and the column $x_c$, the free space
allowing for the contrac-
tion. The experimental
values of the viscosity are
taken from the paper of
Thorpe and Rodger.[4]

The values of $K$ calcu-
lated from these figures for
the 51·92 molecular percen-
tage are given in Table VII.

Allowing for the diverg-
ence of the above figures from equimolecular proportions and for the
fact that an error of 1 per cent. in observed or calculated values of the

TABLE VII.

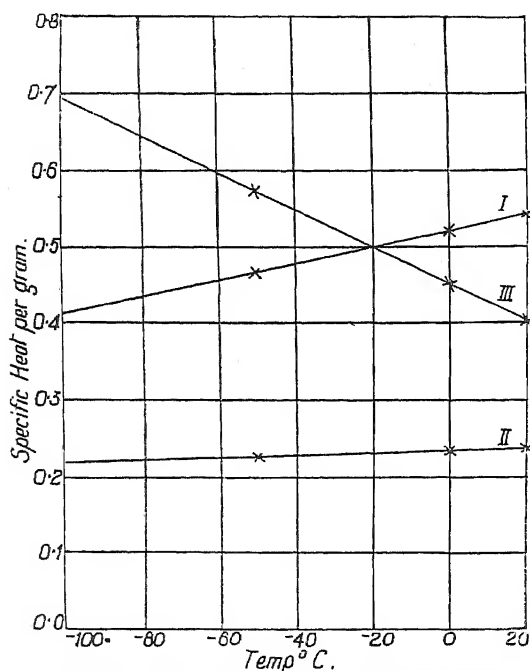| Temp. °C. | $a.$ | $b.$ | $K.$ |
|---|---|---|---|
| 0 | 0·585 | 0·542 | 0·014 |
| 10 | 0·577 | 0·534 | 0·021 |
| 20 | 0·569 | 0·527 | 0·030 |

viscosity is equivalent to an error of 10 per cent. in the value of the combined molecules, these values correspond to 25 to 27 per cent. of the molecules being combined at 0°, 20 to 22 per cent. at 10° and 16 to 18 per cent. at 20° C.

The heat of reaction calculated from the relation

$$\frac{d \log K}{dT} = \frac{Q}{RT^2}$$

between 0° C. and 20° C. gives a value of 6070 Cals. per gram molecule. This would correspond to an experimental value of about 1500 Cals. at 0° C. and 1250 Cals. at 10° C., which is close to the value determined experimentally.

There is another way in which the heat of reaction might be obtained approximately. It has been shown by Smits and Berckmans,[5] that at − 94° C. a compound of ether and chloroform crystallises out from an equimolecular mixture. At this temperature, we might take it, 100 per cent. of the molecules are combined. Knowing the heat of reaction at ordinary temperatures and the specific heats of the pure constituents and of the mixture at various temperatures down to any given temperature, it is possible to calculate the heat of reaction over the above range of temperature. The specific heats of ether and chloroform and an equimolecular mixture are already quoted earlier in the paper from Dolazalek and Schulze. They are shown graphically in Fig. 3. They all appear to lie, practically, on straight lines. The mean values between 20° C. and − 94° C. are 0·48 for ether, 0·23 for chloroform and 0·54 for the equimolecular mixture. The difference, therefore, in the heat content for 193·5 grams of the mixture between 20° C. and − 94° C. and 1 gram molecule of ether and one of chloroform for the same range of temperature is equal to



[I] Ether. [II] Chloroform. [III] Equimolecular mixture.

FIG. 3.

$$[0\cdot54 \times 193\cdot5 - 0\cdot48 \times 74 - 0\cdot23 \times 119\cdot5]114 = 4730 \text{ Cals.}$$

5 Proc. Roy. Acad. Sci., Amsterdam, 1918, 401, 21.

Taking the heat of reaction at 20° as 1150 Cals., this would give the heat of reaction at complete combination as

$$4730 + 1150 = 5880 \text{ Cals.},$$

which is practically the value obtained previously.

Dolezalek from a study of the vapour pressures of ether and chloroform mixtures,[6] concludes that at 19° C. about 24 per cent. of the molecules are combined.    This is a slightly higher percentage than that found in this paper.    In the analysis of the viscosity of binary mixtures, the importance of the change of volume on mixing has been stressed. It is not difficult to show that this change of volume is also important in discussing other physical properties of mixtures.    The contraction for equimolecular mixtures of ether and chloroform is equal to 1·25 per cent. of the original volume.    We might expect, therefore, that this represents an increase of internal cohesion throughout the liquid of the same order.    As a vapour molecule has to overcome the internal cohesive forces to escape, a reduction of 1·25 per cent. in the vapour pressure would be due to the greater internal forces after mixing.    The calculated vapour pressure of an equimolecular mixture of ether and chloroform at 19° C. is about 320 mm.    A reduction of 1·25 per cent. would be equivalent to a reduction of 4 mm.    As the total observed reduction is 75 mm. approximately, this represents 5 to 6 per cent. of the total.

Dolezalek and Schulze [3] from a study of the contraction on mixing ether and chloroform vapours at 80° C. and 100° C., deduce the percentage of combined molecules in the liquid condition.    In this paper they appear to obtain 33 per cent. of combined molecules at 20° C., but this value seems higher than is warranted by a study of the heats of reaction. The above authors use the values they have obtained to calculate the viscosity of ether-chloroform mixtures at 20° C.    It is certain, however, that the expression they use to calculate their mixtures, namely,

$$\eta = \eta_a V_a^2 + \eta_c V_c^2 + 2\eta_9 V_a V_c$$

where      $\eta_9 = \sqrt{\eta_a \eta_c}$

is of doubtful value, as it fails to give satisfaction when applied to an ideal mixture.

## Conclusions.

1. The heats of reaction of ether-chloroform mixtures at 3° C., 15° C., and 24° C. and at various percentages are determined experimentally.

2. The results are shown to support the view that a reaction takes place involving one molecule of ether and one of chloroform to form a compound.

3. Deductions indicate that at 15° C. from 15 per cent. to 20 per cent. of the molecules are combined.

We wish to express our indebtedness to the Chemical Department, Canterbury College, for assistance with the experimental work, and to Dr. C. Coleridge Farr, F.R.S., for helpful criticism and advice.

*Canterbury College,*
  *New Zealand,*
    *November,* 1934.

[6] *Z. physik. Chem.*, 1910, **71**, 191.

# MECHANISM OF IONIC REACTIONS.

By Richard A. Ogg, Jr.,[1] and M. Polanyi.

*Received 10th December*, 1934.

This discussion is restricted to monomolecular and bimolecular ionic reactions of the following types, involving a homopolar molecule AB.

1. $XY \rightarrow X^+ + Y^-$ (One bond broken).
2. $Z^- + XY \rightarrow ZX + Y^-$ (One bond broken, one formed).
3. $XY + A^+ \rightarrow X^+ + YA$ (One bond broken, one formed).

These are the simplest possible ionic reactions with respect to the number of linkages broken and formed. Since reactions of these types occur chiefly in the presence of a polar solvent, only such cases will be considered. Under these circumstances (*i.e.*, in solution) in addition to the breaking and formation of atomic linkages, the reactions imply also the disruption and formation of solvation shells. The first example above represents simply an electrolytic dissociation; the second and third have been discussed in previous communications [2, 3] as "negative mechanism" and "positive mechanism" respectively.

We wish to derive the factors governing the rate of reactions of the above type, each of which involves a change of electronic state, by application of the following principle. Throughout the course of the nuclear motions accompanying the change from the initial to the final configuration, the reacting system is in that electronic state having the lowest energy. Failure to obey this principle must necessarily result in a slower reaction. From the admittedly rough review of experimental evidence presented in this and the following communication, there is no need to assume that any ionic reactions known at present constitute exceptions to this rule.

## 1. Electrolytic Dissociation.

The rate of electrolytic dissociation of organic halides can be measured in some cases,[4] and it has been assumed [5] that the hydrolysis of many such halides is governed by an electrolytic dissociation of the carbon-halogen linkage, followed by reaction of the carbonium ion with water.

We will deduce first the treatment of the rate of such electrolytic dissociations. Although the applicability of the treatment is at present

[1] International Research Fellow in Chemistry.
[2] M. Polanyi, "Atomic Reactions," Williams and Norgate, London, 1932; N. Meer and M. Polanyi, *Z. physikal. Chem.*, **19B**, 164, 1932.
[3] E. Bergmann, M. Polanyi and A. Szabo, *Z. physikal. Chem.*, **20B**, 161, 1933.
[4] E. Bergmann and M. Polanyi, *Naturwissenschaften*, **21**, 378, 1933.
[5] Ward, *J. Chem. Soc.*, 2285, 1927; Meerwein, *Lieb. Ann.*, 455, 227, 1927; see also Strauss' work in W. Hückel, *Theoretische Grundlagen der Organischen Chemie*, vol. 2, Leipzig, p. 269, 1931; R. Robinson, *Institute of Chemistry Lecture*, 36, 1932; Extension and further discussion of this view by Ingold and Patel, *J. Chem. Soc.*, 526, 1933; Ingold and Hughes, *Nature*, **132**, 933, 1933.

limited by the lack of experimental evidence it will serve as the simplest means of exposition of the principal factors determining the rate of ionic reactions.

We restrict ourselves to cases in which the heat of dissociation into ions is smaller than of that into neutral fragments. The potential energy curves relevant to the discussion are depicted in Fig. 1. Curve (*a*) represents the potential energy of the homopolar state of the molecule XY as a function of nuclear separation. The form and position of the curve are essentially independent of the presence of the solvent atmosphere, and hence it refers to the molecule either in the gaseous state or in solution. Curves (*b*) and (*b'*) refer to the ionic state $(X^+Y^-)$ in the gas phase and in solution respectively.

Curve (*b*) is a typical potential energy curve for a stable ionic molecule, the right branch being composed chiefly of the coulombic attraction between the charges, and the left branch of the steep repulsive potential resulting from interpenetration of the ions. It is to be noted that the mean internuclear distance of the ionic state is represented as appreciably larger than that for the homopolar state. This arises from the fact that in the cases considered the increase of " diameter " of the atom Y on becoming a negative ion $Y^-$ is greater than the decrease in diameter of X on becoming a positive ion $X^+$.

Curve (*b'*) is derived from (*b*) by superposition of the solvation effects. This lowers the asymptotic value by the sum of the solvation energies for the two ions, and hence brings the ionic state into the same energy region as the homopolar state.



Fig. 1.

In addition to reducing the forces acting between the ions at large distances, the solvent alters the intermediate form of the curve so that repulsion between the ions obtains at moderate separations, causing the heteropolar molecule to be unstable.

The reason for this repulsion between the ions at moderate distances in solution is that their nearer approach requires the removal of part of the solvation shells, with a corresponding increase of potential energy. Alternatively, the effect may be described as an overlapping of the fields of the ions, resulting in a decrease of solvation energy. Hence for the ionic state in solution the potential energy for a nuclear separation corresponding to the stable gaseous heteropolar molecule will be well above its asymptotic value. At very small separations the predominating energy effect, as in the gaseous molecule, is the repulsion due to interpenetration of the ions.

The " crossing " of the potential energy curves (*a*) and (*b'*) (referring to different electronic states) results in the well-known effect that the curves separate in the region of " crossing," forming two resultant curves as indicated by the dotted lines in Fig. 1. The separation of
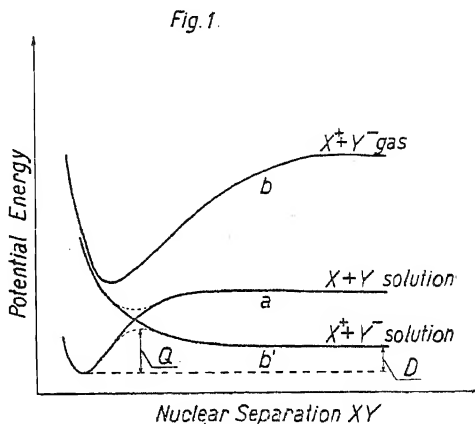
the curves in the neighbourhood of the crossing measures the energy of interaction or " resonance " between the two electronic states.   From the principle cited above the *lower* of the resultant curves represents the actual passage of the system from the initial to the final state ; the maximum in the neighbourhood of the " crossing " corresponds to the *transition state*, the height ($Q$) of the curve at this point being the activation energy.   The excess ($Q - D$) of activation energy over the endothermicity might be considered as the true activation energy of the electrolytic dissociation.   This is of course also the activation energy for the reverse process, the union of the two ions to form a homopolar molecule.

Consideration of the foregoing discussion and of the curves in Fig. 1 reveals three important effects contributing to the true activation energy for the electrolytic dissociation of a homopolar molecule in solution.

(1) The increase in effective diameter attending the change of the neutral dissociation fragments into ions requires a preliminary extension of the homopolar linkage to accommodate this change, the corresponding increase of potential energy appearing in the activation energy.

(2) The second effect involves the solvent specifically.   The change of the atomically bound fragments into ions must necessarily take place at rather small nuclear separations.   Hence the fields of the resulting ions will quite largely overlap, with the result that the solvation energy will be considerably less than at large separations.   This means an increase of the potential energy of the transition state, and hence an increased activation energy.

(3) The interchange or resonance between the two electronic states (homopolar and ionic) lowers the potential energy of the transition state, and results in a decrease in activation energy.

From the above it appears very probable that many such electrolytic dissociations must be attended by true activation energy.   Experimental evidence is as yet inadequate to allow of a decision concerning this point.

The value of the above discussion lies in the deduction and illustration of important factors determining the activation energy and rate not only of electrolytic dissociation, but also (as will appear subsequently) of ionic reactions in general.   It thus introduces the more extended treatment of the other examples given at the beginning.

### Negative Ion Reactions.

Abundant examples are known of negative ion reactions, and many careful studies have been made of the kinetics of such changes.   The great majority of such studies deal with reactions involving alkyl halides, and hence special attention will be paid to these.   Reactions of alkyl halides with negative ions have been discussed previously [1] and it was pointed out that during such a reaction the approach of the negative ion is toward the positive end of the carbon-halogen dipole, a process leading to optical inversion if the carbon atom is asymmetric.   It likewise appears that this approach will be most probable along the line joining the carbon and halogen nuclei :

The reaction :          $Z^- + XY \rightarrow ZX + Y^-$

bears many points of resemblance to the case of electrolytic dissociation, a resemblance that is made clearer by using a similar graphic representation of the potential energy functions of the two electronic states involved. As is pointed out above in the configuration leading to reaction the nuclei of X, Y and Z are colinear. Hence the potential energy is a function of two co-ordinates only, the separations ZX and XY giving potential energy surfaces. If, however, a fixed value of ZX is chosen, the energy is a function of XY alone. The resulting two-dimensional curves are simply cross-sections of the potential energy surfaces at the value chosen for the co-ordinate ZX. The essential form of the curves is illustrated [5a] in Fig. 2.

Curve $(c)$ in Fig. 2 refers to the homopolar molecule XY in the presence of the solvent medium and with the ion $Z^-$ at some fixed distance ZX' from X. The form of the curve is assumed to be the same as that for the gaseous molecule. Hence interaction with the solvent and with the ion $Z^-$ has only the effect of shifting the entire curve vertically. Curve $(e)$, which to avoid complication of the diagram is not drawn in full, represents the position of curve $(c)$ corresponding to $ZX' = \infty$.

It is obvious that curve $(e)$ represents the initial state of the reacting system.

Curve $(d)$ refers to the energy of interaction between the ion $Y^-$ and the homopolar molecule ZX (the nuclear separation of which is equal to ZX') in the presence of the solvent. Since the form of the potential energy function for ZX is also assumed to be the same as that for the gaseous molecule, it is clear that a change in ZX does not



Fig. 2.

affect the form of curve $(d)$, but merely shifts it vertically. Curve $(f)$, likewise not drawn in full, represents the position of curve $(d)$ corresponding to ZX' equal to the normal internuclear distance in ZX. It is evident that the asymptotic value of curve $(f)$ represents the final state of the reacting system.

The "crossing" of the curves $(c)$ and $(d)$ has the same effect discussed in connection with electrolytic dissociation, and the resultant curves are indicated by the dotted lines. As before, the lower curve represents a passage of the system from one state to another, the quantity $Q'$ being the minimum energy increment necessary for this passage. A point to be emphasised is that in this diagram the relative position of the curves $(c)$ and $(d)$ is dependent upon the corresponding value fixed upon for ZX. To each value of ZX there will correspond a certain passage and some value of $Q'$. Of this infinite set of values

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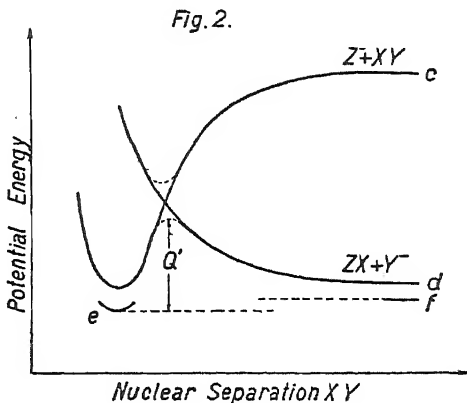
[5a] Fig. 2. gives (when an appropriate scale is assumed for the co-ordinates) an approximate presentation of the examples listed in the second half of Table III.

Fig. 1 also relates to the alkyl halides, the co-ordinate scales being adjusted appropriately.

of $Q'$ there will be a minimum value $(Q')_{Min}$, corresponding to the lowest passage. The general principle stated earlier leads us to identify $(Q')_{Min}$ with $Q$, the activation energy of the reaction. As before, the true activation energy is $Q - D$, where $D$ represents the heat of reaction.

There is thus seen to be a close similarity between the mechanism of negative ion substitution and that of electrolytic dissociation, reflected in a similarity of the factors affecting their respective activation energies. In particular, the first and third factors mentioned at the close of the discussion on electrolytic dissociation apply unchanged to negative ion reactions. That is, the change of atom Y to a negative ion is attended by an increase of " effective size," the separation of the steep left branches of curves $(c)$ and $(d)$ in Fig. 2, corresponding to this increase. A preliminary elongation of XY is necessary to accommodate the change, the corresponding expenditure of work appearing as activation energy. Likewise the interchange or resonance between the electronic states represented by $(c)$ and $(d)$ results in a decrease of potential energy in the transition state, and hence in a diminished activation energy.

In the case of negative ion reactions the effect of the solvent upon the activation energy is simpler than in that of electrolytic dissociation. In order for the reaction to occur the molecule XY must penetrate the solvation shell of the ion $Z^-$. The result is to cause an upward displacement of curve $(c)$ in Fig. 2 by the corresponding energy difference. Likewise in the transition state ZX must occupy a position in the solvation shell of ion $Y^-$, with the result that the form of curve $(d)$ is altered in the neighbourhood of the " crossing "—an increase in potential energy being produced. The net effect is to cause an increase of activation energy which is greater the stronger the solvation of the ions.

Finally, in negative ion reactions involving alkyl halides there is a fourth factor contributing to activation energy which does not appear at all in electrolytic dissociation. This factor arises from the optical inversion attending the reaction. It appears that in the transition state the other three valences of the carbon atom must be displaced from their normal tetrahedral position to one in which they can be approximately in a plane perpendicular to the line of approach of the attacking ion. This displacement of the carbon substituents of course requires an expenditure of energy. The effect is to cause a corresponding upward shift of curve $(c)$ in Fig. 2, and a change in the form of curve $(d)$ in the neighbourhood of the " crossing," resulting in an increase of potential energy. Hence the overall result is simply to increase the activation energy by the energy required to displace the carbon substituents from their normal positions to those occupied in the transition state.

The above four factors give an essentially complete description of the activation energy of negative ion reactions, and an evaluation of these factors should allow the actual calculation of the activation energy in a specific case. We wish to show how an approach to this procedure may be made for certain simple reactions, and to deduce some generalisations relating to various ionic reactions whose kinetics have been subjected to experimental study.

The procedure of the calculation amounts simply to the evaluation of the energy functions represented by curves $(c)$ and $(d)$ (Fig. 2) as functions of the internuclear distances ZX and XY, estimation of the numerical values of $Q'$, and the finding of the minimum value of $Q'$, i.e., $Q$ by trial. It should be emphasised that for this purpose it is not

necessary to know the form and position of the entire energy curves, but merely of the relevant portions, *i.e.*, in the neighbourhood of the initial and final states and especially of the transition state (the region of the " crossing " of the curves). This is a considerable convenience, as the intermediate portions of the curves, especially of curve $(d)$, may be very difficult to evaluate.

We shall denote by $E_1$ (ZX, XY) and $E_2$ (ZX, XY) respectively the energy functions represented by curves $(c)$ and $(d)$ in Fig. 2. As stated previously it is assumed that the form of the potential energy curves for the homopolar molecules is not affected by their environment. Likewise, it is assumed that elongation of the homopolar linkages does not affect the energy of interaction with the ions and solvent.

The further assumption is made that both of these energies are independent of the interchange or resonance energy between the two electronic states. These three assumptions are embodied in the equations (1) and (2)

$$E_1 \text{ (ZX, XY)} = E_a \text{ (ZX)} + E_b \text{ (XY)} \pm \tfrac{1}{2}W \quad . \quad . \quad (1)$$
$$E_2 \text{ (ZX, XY)} = E_b \text{ (ZX)} + E_a \text{ (XY)} \pm \tfrac{1}{2}W \quad . \quad . \quad (2)$$

Here $E_b$ (XY) and $E_b$(ZX) represent respectively the energy functions for the homopolar molecules XY and ZX, while $E_a$(ZX) and $E_a$(XY) are the interactions with the solvent and the respective ions $Z^-$ and $Y^-$. $W$ is the resonance energy. The alternative sign of $W$ produces the two resultant curves in Fig. 2. As stated before, we are concerned only with the lower of these curves, and hence for the calculations $W$ is always negative in the above equations.

In Fig. 2, $E_b$(XY) determines the form of curve $(c)$ and $E_a$(ZX) its position. Likewise $E_a$(XY) determines the form of curve $(d)$ and $E_b$(ZX) its position.

The functions $E_a$(ZX) and $E_a$(XY) need be evaluated only in the neighbourhood of the transition state. In the transition state we consider the homopolar molecule (which we shall take as an alkyl group bound to a negative substituent) to have replaced one solvent molecule in the solvation shell of the ion, and that the other substituents of the carbon atom are displaced as described previously. The energy required to dissociate completely one molecule of the solvent from the ion is denoted as $S$; that required to force the three valences of the carbon atom into the planar configuration is denoted as $N$; and the energy of interaction of the ion and homopolar molecule we designate as $L$. These energy factors are taken as independent and hence

$$E_a(\text{ZX}) = L(\text{ZX}) + S_z + N$$
$$E_a(\text{XY}) = L(\text{XY}) + S_y + N$$

$L$ is composed of three terms. The first of these, designated as $\gamma$, represents interaction of the charge on the ion and the dipole of the carbon bond attacked (*i.e.*, between the ion $Z^-$ and the bond $C - Y$ or between the ion $Y^-$ and the bond $C - Z$). The second term, $\delta$, denotes the energy of polarisation of the carbon atom in the field of the ionic charge (of the ion $Z^-$ or $Y^-$). The third, $\rho$, is the repulsion caused by mutual interpenetration of the carbon atom and the ion ($Z^-$ or $Y^-$). Then,

$$L(\text{ZX}) = \gamma\text{ZX} + \delta\text{ZX} + \rho_z$$
$$L(\text{XY}) = \gamma\text{XY} + \delta\text{XY} + \rho_y.$$

## Numerical Illustration of Theory.

The quantitative verification of the above theory by calculation of the absolute value of the activation energy is not to be accomplished in the present state of knowledge concerning the factors involved. It will, however, be shown that the most plausible assumptions concerning these factors yield activation energies close to these observed experimentally for negative ionic reactions, and that the differences between the observed and calculated values may be attributed to the unavoidable uncertainty in the numerical values assumed. Furthermore, it will appear that the sequence and successive differences of activation energies (as for example in a series of ionic reactions involving the different halide ions) is given with satisfactory precision by the theory.

## General Procedure.

**Evaluation of $E_b(XY)$ and $E_b(ZX)$.**—The molecules XY and ZX, which in the cases considered are really polyatomic, are treated as essentially diatomic, *i.e.*, the radicals X, Y and Z are regarded as rigid with regard to extension of the linkages in question. Then for the functions $E_b(XY)$ and $E_b(ZY)$ we can employ the function given by Morse [6] for the binding energy of a diatomic molecule. For example

$$E_b(XY) = D_{xy} - E_{\text{Morse}}$$
$$E_{\text{Morse}} = D_{xy}(2e^{-a(r-r_0)} - e^{-2a(r-r_0)}).$$

$D_{xy}$ represents the dissociation energy of XY, $r$ its nuclear separation (*i.e.*, $XY = r$), and $r_0$ the normal value of $r$. "$a$" is equal to $0 \cdot 1227\ \omega_0\sqrt{\dfrac{M}{D}}$ where $\omega_0$ is the "fundamental vibration frequency" and $M$ the reduced mass $\dfrac{M_1 M_2}{M_1 + M_2}$.

## Evaluation of $L(xy)$ and $L(zx)$.

**1.** The value of $\gamma$ is found as follows. If the dipole moment of the $\overset{\smile}{\underset{|}{C}} - Y$ linkage is denoted by $\mu_{xy}$, and $\epsilon$ represents the charge on the electron, then

$$\gamma_{zx} = -\ \frac{\epsilon\mu_{xy}}{(XY+\Delta)^2}.$$

A similar expression obtains for $\gamma_{xy}$, using $\mu_{xz}$. $\Delta$ is a distance localising the dipole at a point in the bond. It is assumed that the dipole is located at the "junction" of the two atoms constituting the bond. Hence $\Delta$ is equal to the well-known radius of the carbon atom, *i.e.*, $0 \cdot 77 \times 10^{-8}$ cm.

**2.** In calculating $\delta$, if $\alpha$ is the polarisability of the carbon atom, then

$$\delta_{zx} = -\frac{\alpha}{2}\ \frac{\epsilon^2}{(ZX)^4}$$

and similarly for $\delta_{xy}$. The polarisability of carbon is calculated from

[6] H. Morse, *Physic. Rev.*, **34**, 37, 1929.

the atomic refraction of carbon in organic compounds for light of infinite wave-length.

$$\alpha = \frac{3P_{\infty}}{4\pi N}$$

where $P_{\infty}$ is the atomic refraction and $N$ Avogadro's number. The required value of $P_{\infty}$ was obtained by extrapolation to $\lambda = \infty$ of the values given by Hückel [7] using the customary Cauchy formula. The value so obtained is 2·37 c.c. and the corresponding polarisability is $\alpha = 9·3 \times 10^{-25}$.

**3.** The term $\rho$, *i.e.*, the energy of repulsion, is due to interaction of the electronic structures of the ion and of the carbon compound, and the consequent quantum mechanical exchange effect, *i.e.*, it is the usual non-electrostatic repulsion. The basis of the treatment of $\rho$ is a consideration of the repulsive forces between ions in crystals, and what amounts to an interpolation to find the corresponding forces between ions and uncharged atoms.

If van der Waals forces are neglected the expression : [8]

$$E = -a\frac{\epsilon^2}{r} + be^{-r/p}$$

gives the potential energy per molecule of a regular crystal lattice composed of anions and cations of charges $+ \epsilon$ and $- \epsilon$ separated by a distance $r$. The first term gives the energy due to the electrostatic attraction, "$a$" being the Madelung constant. The second term represents the energy of repulsion. The coefficient $b$ can be evaluated from the fact that at the equilibrium separation $(r = r_0)$, $\frac{dE}{dr} = 0$,

therefore $$b = ap\frac{\epsilon^2}{r_0^2}e^{r_0/p}.$$

If the repulsion be considered as due solely to anion-cation contact and the number of such contacts (dependent on the lattice type) per ion is $K$ then the repulsive energy of an anion-cation *pair* is given by

$$E = b_0 e^{-r/p},$$
where $$b = Kb_0.$$

Hence to evaluate the repulsion between a given pair of ions it is necessary to know only the corresponding values of $r_0$ and $p$ (for a certain lattice type). In the cases to be considered we shall assume for $p$ the value of $0·345 \times 10^{-8}$ cm. which Born and Mayer [8] found as the average for seventeen alkali halides, with only slight deviations.

Pauling [9] has derived a set of single ionic radii to be used in crystal lattices of the NaCl type. For a given pair of ions the sum of the corresponding radii gives $r_0$ for such a lattice. For the polyvalent ions and rare gas atoms he gives also so-called "univalent radii" which are the effective radii which the ions would possess if singly charged, but unaltered in electronic structure. It is these latter values that give the best idea of the actual extension of the ions in space.

From the above principles we can derive some idea of the magnitude

[7] W. Hückel, *Theoretische Grundlagen der Organischen Chemie*, Leipzig, 1931, vol. II., p. 94.
[8] M. Born and J. E. Mayer, *Z. Physik*, **75**, 1, 1932.
[9] L. Pauling, *J. Am. Chem. Soc.*, **49**, 771, 1927.

of the repulsion between a halogen ion and a combined carbon atom, as in a methyl halide. This repulsion is assumed to be given by the above expression $b_0 e^{-r/p}$ and it remains to evaluate $b_0$. (The use of such an expression for repulsion is justified by quantum mechanics.) The data of Pauling and the above value of $p$ allow the calculation of the repulsion between a given halogen ion and the $C^{4+}$ ion (univalent radius $= 0.29 \times 10^{-8}$ cm.) as well as between a halogen ion and neon atom (univalent radius $= 1.12 \times 10^{-8}$ cm.). It appears that the case of a halogen ion and carbon atom is intermediate between these two extremes, since the electronic structure of carbon ($2K$ electrons, $4L$ electrons) is intermediate between that of $C^{4+}$ ($2\ K$ electrons) and Ne ($2\ K$ electrons, $8\ L$ electrons) and hence, that the univalent radius of carbon is between 0.29 and $1.12 \times 10^{-8}$ cm. However, apparently a substituted carbon atom (which, of course, has a completed shell) more nearly approaches the case of neon. In fact a neon atom would result if the four hydrogen nuclei in methane were merged into the carbon nucleus.

With these considerations in mind, we shall arbitrarily choose the " univalent radius " of substituted carbon as $1.00 \times 10^{-8}$ cm. Adding this value to the radii given by Pauling for the halogen ions, and using the resulting values of $r_0$ in the above formula, we derive the corresponding coefficients in the expression for the repulsive energy. (It should be noted that for the NaCl type lattice the value of the Madelung constant is 1.748 and the number of anion-cation contacts per ion is six.)

**Evaluation of** $S$ : The quantity $S$, representing the interaction of a single solvent molecule with the negative ion, may be represented by a function analogous to $L$ described above, which we term $L_s$

$$L_s = \gamma_s + \delta_s + \rho_s.$$

For equilibrium the derivative of this quantity with respect to the distance $u$ between the ion and the solvent molecule vanishes,

*i.e.,* $$\frac{dL_s}{du} = 0.$$

The solution of this equation for $L_s$ gives the value of $S$.

**The Energy Term** $N$ : required to displace the substituents of the carbon atom from their normal position to the plane configuration required in the transition state cannot be evaluated directly. However, that its magnitude is small can be inferred from the great velocity with which free carbonium ions $R_2—\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{\mid}}C^+$ undergo optical inversion [4] a process that requires passage through such a plane configuration. An actual estimate of the activation energy for this inversional leads to a value of two or three kilogram calories, as the upper limit for $N$.
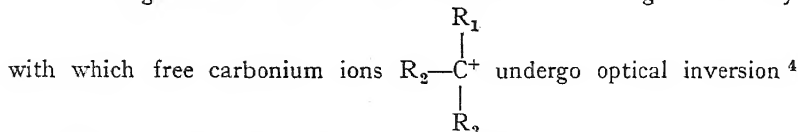
**The Energy Term** $W$ : This term represents interchange energy between two saturated electronic structures, *i.e.*, between a negative ion and an alkyl radical, bound to a negative substituent. Essentially these may both be considered to be the noble gas type. The van der Waals forces between structures of this sort are due to such terms as $W$, and hence we may conclude that $W$ is probably of the order of magnitude

of these van der Waals forces, *i.e.*, at most a thousand or so gram calories per mole. Such a value of $W$ would be sufficient to ensure a transition probability close to unity so that the system would actually follow the lower of the resultant curves in Fig. 2. At the same time the calculated activation energies would not be significantly lowered.
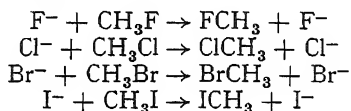
## Reactions of Halogen Ions with Alkyl Halides.

These reactions are chosen as examples because the systematic evidence relating to them is comparatively extensive, and also because the treatment outlined above is most readily applied in the calculation of the activation energy of such reactions.

Cases are known of these reactions in which the halide ion and the halogen atom substituted by it are identical. The most extensive evidence relates to racemisation of optically-active iodides by iodide ions in acetone solution.[2] Likewise, there are many examples of true chemical substitution. The most of these deal with reactions of iodide ions with alkyl chlorides in acetone solution.

As a simplification the calculations will be carried out for reactions of halide ions with methyl halides in acetone solution. Extension of the results to reactions involving other alkyl halides, and to other solvents will be discussed below.

Activation energies are calculated for two groups of reactions ; first, what we may term identical substitutions,

$$F^- + CH_3F \to FCH_3 + F^-$$
$$Cl^- + CH_3Cl \to ClCH_3 + Cl^-$$
$$Br^- + CH_3Br \to BrCH_3 + Br^-$$
$$I^- + CH_3I \to ICH_3 + I^-$$

and secondly, a number of true chemical substitutions.

$$I^- + CH_3F \to ICH_3 + F^-$$
$$I^- + CH_3Cl \to ICH_3 + Cl^-$$
$$I^- + CH_3Br \to ICH_3 + Br^-.$$
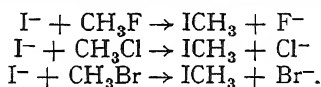
Reactions of the first group are more readily dealt with. In these the molecules ZX and XY are identical, the heat of the reaction is zero, and the transition state is symmetrical, *i.e.*, $(ZX)_{crit.} = (XY)_{crit.}$. Therefore equations (1) and (2) become identical, and the potential energy of the transition state is given by,

$$[E_1(ZX, XY)]_{min.} = [E_1(XY, XY)]_{min.} = (E_a(XY) + E_b(XY) - \tfrac{1}{2}W)_{min.}$$
$$= [E_b(XY) + \gamma_{xy} + \delta_{xy} + \rho_{xy}]_{min.} + S + N - \tfrac{1}{2}W.$$

Since the initial state is taken as the zero of the potential energy, the above expression is equal to $Q$, the activation energy. The minimum value of $[E_b(xy) + \gamma_{xy} + \delta_{xy} + \rho_{xy}]$ is easily found by trial.

Reactions of the second group are more complicated. In general such true chemical reactions have a heat of reaction. However, for the enumerated cases it appears that the heats of reaction in acetone solution must be very small, and we shall assume them to be zero. It is obvious that in such reactions the transition state is unsymmetrical. Nevertheless, the energy quantities represented in equations (1) and (2) must be identical for this state. That is

$$[E_1(ZX, XY)]_{min.} = [E_2(ZX, XY)]_{min.} = Q.$$

The values satisfying this equation are found by plotting on co-ordinate paper curves of $ZX$ against $XY$, each representing some constant value of $E_1(ZX, XY)$ or $E_2(ZX, XY)$. There are thus two sets of curves, each set representing contour lines of the respective potential energy *surfaces* corresponding to the two functions. The value of the energy for which the corresponding contour lines of the two sets are tangent gives the solution of the above equation, *i.e.*, the value of the activation energy.

**List of Data Employed.**—In computing the Morse functions of the methyl halides, and the values of $E_b$ $(XY)$ and $E_b$ $(ZX)$, the methyl group is assumed to be a rigid unit with a mass of 15. The values of $\omega_0$ are taken as the Raman frequencies corresponding most closely to the longitudinal vibration of the carbon halogen linkage.[10] The list of the quantities is given in Table I.

TABLE I.

| Molecule. | D-Kilo Cals. per Mole. | $\omega_0$ cm.$^{-1}$. | $M$. | $a$. | $r_0$. |
|---|---|---|---|---|---|
| CH$_3$F . . | 126 [11] | 1049 | 8·38 | 1·97 | 1·41 [12] |
| CH$_3$Cl . | 73 | 712 | 10·55 | 1·77 | 1·85 [13] |
| CH$_3$Br . | 59 | 603 | 12·63 | 1·83 | 2·06 [14] |
| CH$_3$I . . | 44 | 534 | 13·40 | 1·95 | 2·28 [14] |

In computing $\gamma$ the following values have been used for the dipole moment, $\mu$ of methyl fluoride, chloride, bromide and iodide respectively, 1·80 [15] 1·85 [15] 1·45 [16] and 1·35 [16] e.s.u.

For $\delta$ the value $9 \cdot 3 \times 10^{-25}$ cm.$^3$, explained above, was used for the polarisability of carbon.

The data for $\rho$ are given in Table II.

TABLE II.

| System. | Univalent Ionic Radii. | | $p$. cm. | $b_0$-Kilo Cals. Per Mol. |
|---|---|---|---|---|
| | Halogen Ions [9] cm. | Carbon cm. | | |
| F$-$ + C . | $1 \cdot 36 \times 10^{-8}$ | $1 \cdot 00 \times 10^{-8}$ | $0 \cdot 345 \times 10^{-8}$ | $5 \cdot 57 \times 10^3$ |
| Cl$-$ + C . | 1·81 | $1 \cdot 00 \times 10^{-8}$ | $0 \cdot 345 \times 10^{-8}$ | $1 \cdot 425 \times 10^4$ |
| Br$-$ + C . | 1·96 | $1 \cdot 00 \times 10^{-8}$ | $0 \cdot 345 \times 10^{-8}$ | $1 \cdot 903 \times 10^4$ |
| I$-$ + C . | 2·16 | $1 \cdot 00 \times 10^{-8}$ | $0 \cdot 345 \times 10^{-8}$ | $3 \cdot 14 \times 10^4$ |

In calculating $S$, the appropriate value of $\gamma$ is computed from the value of $2 \cdot 75 \times 10^{-18}$ e.s.u. for the dipole moment of acetone.[17] $\delta$ and $\rho$ are taken to be the same as above.

[10] W. D. Harkins and H. E. Bowers, *Physic. Rev.*, 38, 1852, 1931.
[11] H. G. Grimm, *Handbuch der Physik*, 24, 536, 1927.
[12] R. Mecke, *Leipziger Vorträge*, 1931.
[13] R. Wierl, *Ann. Physik*, (5), 8, 521, 1931.
[14] R. W. Dornte, *J. Chem. Physics*, 1, 630, 1933.
[15] C. P. Smyth and K. B. McAlpine, *J. Physics*, 1, 190, 1933.
[16] S. U. Morgan and H. H. Lowry, *J. Physic. Chem.*, 34, 2385, 1930
[17] K. L. Wolf and E. Lederle, *Physik. Z.*, 29, 948, 1928.

## Calculated Activation Energies.

In Table III. are given the results of the calculations for the two groups of reactions. The quantities $(ZX)_{crit.}$ and $(XY)_{crit.}$ refer to the respective carbon halogen separations in the transition state. All the energies are in kilocalories per mole, and distances in cm. $\times 10^{-8}$.

TABLE III.—CALCULATED ACTIVATION ENERGIES.*

| Reaction. | $(XY)_{crit.}$ | $(ZX)_{crit.}$ | $\gamma_{xy}$ | $\gamma_{zx}$ | $\delta_{xy}$ | $\delta_{zx}$ | $\rho_{xy}$ | $\rho_{zx}$ | $E_b(XY)$. | $E_b(ZX)$ | $S_y$. | $S_z$. | $Q$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $F^- + CH_3F$ . | 1·56 | — | −22·9 | — | −25·7 | — | +61·2 | — | +8·0 | — | +18·8 | — | +39·4 |
| $Cl^- + CH_3Cl$ . | 2·15 | — | 15·1 | — | 7·2 | — | 28·0 | — | 12·5 | — | 13·3 | — | 31·5 |
| $Br^- + CH_3Br$ . | 2·36 | — | 10·1 | — | 5·0 | — | 20·7 | — | 10·3 | — | 12·1 | — | 28·0 |
| $I^- + CH_3I$ . | 2·58 | — | 8·3 | — | 3·5 | — | 17·6 | — | 8·6 | — | 10·6 | — | 25·0 |
| $I^- + CH_3F$ . | 1·76 | 2·61 | 14·6 | 10·9 | 16·0 | 3·4 | 33·7 | 16·4 | 18·8 | 9·9 | 18·8 | 10·6 | 31·6 |
| $I^- + CH_3Cl$ . | 2·18 | 2·56 | 10·7 | 11·6 | 7·6 | 3·6 | 25·7 | 18·7 | 14·4 | 7·8 | 13·3 | 10·6 | 28·5 |
| $I^- + CH_3Br$ . | 2·34 | 2·55 | 9·5 | 9·1 | 5·1 | 3·7 | 21·4 | 19·3 | 9·4 | 7·6 | 12·1 | 10·6 | 26·5 |

* In this table, $Q = \gamma_{xy} + \delta_{xy} + \rho_{xy} + E_b(ZX) + S_y$
$= \gamma_{zz} + \delta_{zx} + \rho_{zx} + E_b(XY) + S_z.$

## Comparison of Results with Experiment.

These activation energies are subject to correction by addition of the appropriate values of $N$, and subtraction of $\frac{1}{2}W$. As appeared in the foregoing discussion, both of these quantities are probably small, and since they are opposite in sign we shall assume that their net effect is negligible.

The experimental results with which the calculated activation energies may be compared are listed in Table IV.

It will be observed that none of the experimental results deal with the reactions to which the calculated activation energies refer, and hence we must consider to what extent the results can be compared. The substitution of one or more of the hydrogen atoms in a methyl halide by alkyl or other groups affects the activation energy of the reactions considered here in two ways; first, there is the change in the energy of the carbon-halogen linkage, which is probably always a decrease, but certainly a marked one, only when one or more of the substituents is negative in character, or when a tertiary halide results. This effect results in a corresponding decrease in activation energy. Secondly, the substitution causes the value of $\rho$, the repulsive potential, to increase, and so increases the activation energy. This effect should be marked only when the substituents are voluminous or when tertiary compounds are formed (" steric hindrance ").

Hence, it appears that the activation energies calculated for the reactions of methyl halides should apply also to those involving simple primary and secondary alkyl halides. It will be observed that the values

TABLE IV.—Experimental Activation Energies.

| Reaction. | Solvent. | Activation Energy, Kilocals/Mole. |
|---|---|---|
| Cl-+ $d$-$C_6H_5CH_3CHCl$ [18] | $(CH_3)_2CO$ | 20·9 [23] |
| Cl-+ $d$-$C_4H_9CH_3CHCl$ [18] | $(CH_3)_2CO$ | 23·7 [23] |
| Cl-+ $d$-COOH—CHCl—$CH_2COOH$ [19] | $H_2O$ | 22·8 [23] |
| Br-+ $d$-COOH—CHBr—$CH_2COOH$ [20] | $H_2O$ | 19·2 [23] |
| I-+ $d$-$C_3H_7CH_3CHI$ [18, 3] | $(CH_3)_2CO$ | 17·6 |
| I-+ $d$-$C_4H_9CH_3CHI$ [18, 3] | $(CH_3)_2CO$ | 16·3 |
| I-+ $d$-$C_4H_9CH_3CHI$ [18, 3] | $(CH_3)_2CO + 5\ °/_o\ H_2O$ | 17·4 [23] |
| I-+ $d$-COOH—CHI—$CH_2COOH$ [20] | $H_2O$ | 17·3 [23] |
| I-+ $C_4H_9CH_3CHF$ [18] | $(CH_3)_2CO$ | 23·1 [23] |
| I-+ $C_4H_9CH_3CHCl$ [18] | $(CH_3)_2CO$ | 21·8 [23] |
| I-+ $CH_3(CH_2)_2CH_2Cl$ [21] | $(CH_3)_2CO$ | 23·5 |
| I-+ $ClCH_2$—COOH [22] | $H_2O$ | 19·8 |
| I-+ $C_4H_9CH_3CHBr$ [18] | $(CH_3)_2CO$ | 18·3 [23] |

listed in Table IV. for the activation energies of reactions involving these compounds are some 6-10 kilocalories per mole lower than the activation energies calculated for the corresponding reactions involving methyl halides. We consider this agreement sufficient to attest the essential validity of the theoretical treatment. The differences can all be accounted for by the uncertainty in the numerical assumptions. Indeed, these differences would disappear if in the calculation of $\rho$ we had chosen for the effective radius of the carbon atom instead of $1·00 \times 10^{-8}$ cm. the still plausible value of $0·7 \times 10^{-8}$ cm.

A further test of the theory is afforded by comparison of the activation energy of reactions involving the same alkyl radical in combination with different halogens, and of reactions of a given alkyl halide with different halide ions. It will be observed that not only do the calculations reproduce correctly the sequence of values, but also that they show satisfactory agreement with the experimental differences in activation energy.

The theory predicts that a reaction of the sort considered here will proceed more slowly, the stronger the solvation of the negative ions. This prediction is seen to be confirmed in the experiments on the racemisation of iodides by iodide ions, where the addition of water to the acetone solution decreases the reaction velocity.[24]

[18] A. Szabo, *Dissertation*, Berlin, 1933.
[19] A. R. Olson and F. A. Long, *J. Amer. Chem. Soc.*, **56**, 1294, 1934.
[20] B. Holmberg, *J. pr. Chem.* (2), **88**, 576, 1913.
[21] J. B. Conant and W. R. Kirner, *J. Amer. Chem. Soc.*, **46**, 232, 1924 ; **47**, 476, 1925. The numerous other alkyl chlorides investigated by these authors yield practically identical activation energies in the reaction with iodide ions.
[22] C. Wagner, *Z. physik. Chem.*, **115**, 121, 1925.
[23] These activation energies are computed from the absolute values of the velocity constants, assuming these to be given by the expression

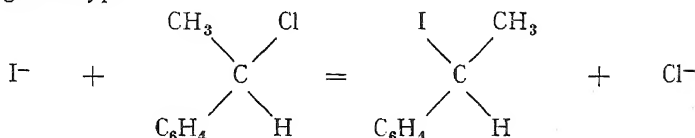$$1·25 \times 10^{10}\, e^{-\,Q/RT}\ \text{sec.}^{-1}\ (\text{mole/liter})^{-1},$$

which fits the results for the racemisation of methylbutyl iodomethane by iodide ions.
[24] The influence which the dielectric constant of a solvent exercises on the rate of a reaction in solution has been outlined in a previous communication by one of us (M. Polanyi, *Z. Electroch.*, **35**, 561, 1929). Whether a reaction goes faster or slower in a solvent of higher dielectric constant, depends on the
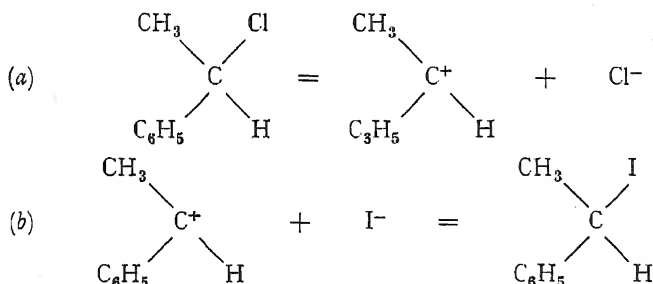
## Negative Substitution and Electrolytic Dissociation.

It is interesting to compare the reaction velocities of electrolytic dissociation with those of negative substitution.    Substitution of

$$\begin{array}{cc} CH_3 & Cl \\ \diagdown\diagup \\ C \\ \diagup\,| \\ C_6H_4 & H \end{array}$$

by $I^-$ in acetone solution is a bimolecular reaction of the "negative type" :

$$I^- \;+\; \begin{array}{cc} CH_3 & Cl \\ \diagdown\diagup \\ C \\ \diagup\diagdown \\ C_6H_4 & H \end{array} \;=\; \begin{array}{cc} I & CH_3 \\ \diagdown\diagup \\ C \\ \diagup\diagdown \\ C_6H_4 & H \end{array} \;+\; Cl^-$$

The same substitution occurs in liquid $SO_2$ in two steps : [25]

$$(a) \quad \begin{array}{cc} CH_3 & Cl \\ \diagdown\diagup \\ C \\ \diagup\diagdown \\ C_6H_5 & H \end{array} \;=\; \begin{array}{cc} CH_3 & \\ \diagdown \\ C^+ \\ \diagup\diagdown \\ C_3H_5 & H \end{array} \;+\; Cl^-$$

$$(b) \quad \begin{array}{cc} CH_3 & \\ \diagdown \\ C^+ \\ \diagup\diagdown \\ C_6H_5 & H \end{array} \;+\; I^- \;=\; \begin{array}{cc} CH_3 & I \\ \diagdown\diagup \\ C \\ \diagup\diagdown \\ C_6H_5 & H \end{array}$$

following the first order the electrolytic dissociation being the rate governing process.

It is known that the electrolytic dissociation of organic halides is stronger in liquid $SO_2$ than in acetone.   This proves that the ions produced are more strongly solvated in liquid $SO_2$ than in acetone.

We have seen that the stronger solvation tends to increase the activation energy of " negative substitution."   On the other hand, a glance at Fig. 1 proves that an increased solvation energy of the ions will cause the ionic curve $(b')$ to be shifted downward and will decrease the activation energy of electrolytic dissociation.

The prevalence in liquid $SO_2$ of the monomolecular reaction over the bimolecular reaction is thus readily accounted for.

Alterations of the organic radical which weaken the $C - Z$ linkage (Z being the group to be replaced in the reaction) will diminish the activation energy of both types of reaction.   However, in the case of the bimolecular substitution such alterations might also cause a steric hindrance which partly offsets or even outbalances the effect of the weakened bond.[2]

energy of the electric field of the " transition state " as compared with that of the initial state.   If the electric field of the transition state contains more energy than that of the initial state, then the rate will be faster in solvents of higher dielectric constants.   In the other case the opposite will be true.   The above is a special application of this theorem.

[25] A study of this reaction has been recently completed by A. Szabo and L. Werner, on the lines put forward in an earlier communication (4).   The results are to be published soon.

It is interesting to note that both the bimolecular substitution of phenyl methyl chloro methane by halogen ions and its electrolytic dissociation are more rapid than the corresponding reactions of secondary aliphatic chlorides.[21, 18, 26]. The weakening of the bond strength prevails here in both reactions.

As a counterpart to this, we might mention that the rate of electrolytic dissociation of benzyl chloride is about ten times *slower* than that of phenyl-methyl-chloro-methane,[27] whereas, it undergoes substitution by $I^-$, very much faster than this compound.[21] We have here a clear case of steric hindrance, caused by the introduction of a methyl group.

The energy of electrolytic dissociation $D_e$, is determined by :

$$D_e = D + I^* - E - S^+ - S^-$$

$D$ homopolar dissociation energy, $I^*$ ionisation energy of free radical, $E$ electron affinity of negative ion, $S^+$ and $S^-$ solvation energies of positive and negative ions respectively.

Alterations of the organic radical do not affect $E$ and $S^-$. Their influence on the electrostatic term $S^+$ will also be small. Alterations of the organic radical must therefore exercise their influence by modifying $D$ and $I^*$ or one of these two terms.

Since variations of $I^*$ have no direct influence on the ease of negative substitution, any change in the rate of these substitutions running parallel to the change in the rate of electrolytic dissociations should rather be attributed to variations of D. We are thus lead to conclude that when substituents increase the electrolytic dissociation, this is caused rather by a decrease of bond strength, than by a decrease in the ionisation energy of the organic radical.

It has been repeatedly suggested that hydrolysis of alkyl halides in cases when its rate is insensitive to the concentration of $OH^-$-ions, might be considered as a process of electrolytic dissociation.[5] The correspondence, when the difference of temperatures are taken in account, of the rate of electrolytic dissociation in liquid $SO_2$, with the rate of hydrolysis in watery alcohol, tends to support this view : For phenyl methyl chloromethane the former process was found to have $k = 4 \cdot 10^{-4}$ at $0°$ C.,[4] while the latter has, according to Ward,[5] $k = 1 \cdot 10^{-2}$ at $50°$ C.

It should be noted that the hydrolysis of optically-active phenylmethyl chloromethane was found by Ward [5] to yield an optically-active product. The sign of rotation of the product, which we might assume to be phenyl methyl carbinol, is opposite to that of the chloride. Since Kenyon, Lipscomb and Phillips [28] have made it very probable that phenyl methyl carbinol and phenyl methyl chloromethane of opposite rotation have opposite configuration, we are led to the conclusion that the hydrolysis is accompanied by optical inversion.

It is easy to recognise that Walden inversion is a necessary concomitant of the electrolytic dissociation of an alkyl halogenide. The transition to the ionic state can only take place if both ions are formed as hydrates ; otherwise the activation heat would be inaccessibly high.[29]
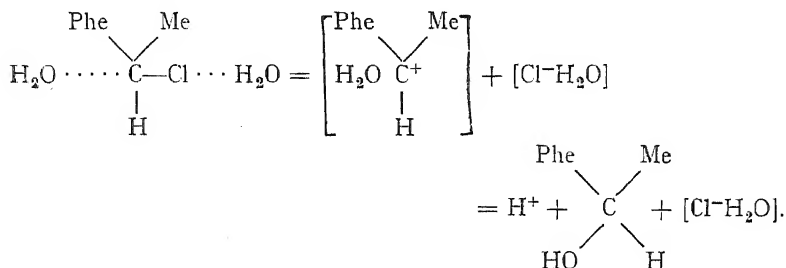
[26] We have found that optically-active sec. butyl iodide does not undergo racemisation even if kept for several days in liquid $SO_2$ at $0°$ C.

[27] Unpublished results of Dr. F. Fairbrother and Mr. A. R. Richards, Manchester.

[28] *J. Chem. Soc.*, 415, 1930.

[29] Since $D_e$ is already very high, an addition to $D_e$ of the order of $S^+$ will carry the value of the activation energy practically out of reach.

At the moment of its formation the carbonium ion can add a water molecule only on its side opposite to the halogen link.   It is to this side, therefore, that the hydroxyl group formed on decomposition of the carbonium hydrate, will become linked to.   The picture of the process is :

$$
\begin{array}{c} \text{Phe} \quad \text{Me} \\ \diagdown \diagup \\ H_2O \cdots C\!-\!Cl \cdots H_2O \\ | \\ H \end{array}
=
\left[
\begin{array}{c} \text{Phe} \quad \text{Me} \\ \diagdown \diagup \\ H_2O \ \ C^+ \\ | \\ H \end{array}
\right]
+ [Cl^- H_2O]
$$

$$
= H^+ +
\begin{array}{c} \text{Phe} \qquad \text{Me} \\ \diagdown \diagup \\ C \\ \diagup \diagdown \\ HO \qquad H \end{array}
+ [Cl^- H_2O].
$$

Attention has been drawn by Ingold [5] to the fact that, while primary aliphatic halides are hydrolysed in a bimolecular mechanism by $OH^-$, the other alkyl chlorides examined until now, proceed by a monomolecular mechanism, that is a process based on electrolytic dissociation. We have already considered above one factor to which such a change over from the bimolecular, to the monomolecular mechanism can be attributed ; the introduction of substituents which combine a weakening of the link $C - Z$ with a steric hindrance.

Another, even more effective factor is found by following consideration.   Suppose an alteration of the organic radical causes $D$ to decrease by some amount $q$ while $I^*$ remains constant.

The change in Fig. 1 will be a downward shift of curve $(b')$ by the amount $q$.   The asymptote of the curve $(a)$ will be lowered to the same extent and this curve will open up correspondingly.   The result will be a lowering of the activation energy by an amount very nearly equal to $q$.

The same decrease of $D$ will cause a decrease of the activation energy of the bimolecular reaction, only by diminishing the term $E\,(XY)$ which has the form,

$$ D(1 - 2e^{-a(r-r_0)} + e^{-2a(r-r_0)}). $$

Assuming that $r$ keeps unchanged, a decrease of $D$ by the amount $q$ will result in a reduction of the activation energy by the quantity,

$$ q(1 - 2e^{-q(r-r_0)} + e^{-2a(r-r_0)}). $$

which is much smaller than $q$.

A decrease in $D$ will therefore facilitate the unimolecular reaction to a greater extent than the bimolecular reaction.   Any such changes (as e.g., in case of benzyl being introduced instead of ethyl) are therefore liable to cause a change-over from the former type of mechanism to the latter one.

We postpone a quantitative treatment of the question until more data will be available.

In conclusion we wish to state that we have gone through all the experimental data concerning substitutions by negative ions, from the point of view of the theory outlined above.

In the course of this review, the following theorem which can be deduced from the mechanism as shown in Fig. 2 became prominent. Suppose the compound XY is substituted by different negative ions

$Z_1^-$, $Z_2^-$, . . . . Suppose the repulsive Term $L(ZX)$ is not very different for these different ions, but the formation energy of the molecules $ZX$ increase in the series $Z_1X$, $Z_2X$, . . . . The main variation in the series of substitutions will then be in the position of $f$, which will shift downward to the extent of the additional exothermicity of each following case. The curve $ZX + Y^-$ will also shift downward by an amount which is readily found from our formula to be nearly equal to the shift of $f$. A downward shift of the curve $ZX + Y^-$ by a certain amount, say $S$, will cause a decrease of the activation energy of the extent $\alpha S$, where the value of $\alpha$ depends on the ratio of the inclinations of the curves $Z^- + XY$ and $ZX + Y^-$, at their crossing point, $\alpha = \frac{1}{2}$ if the inclination of the curves is equal at this point.

It will appear from the theory of prototropic reactions which one of the authors is preparing to put forward in conjunction with J. Horiuti, that an analogous decrease of activation energy with increasing heat of reaction is also marked in prototropic processes. The factor $\alpha$ deduced above will be seen to reappear as the $\alpha$ in Tafel's equation of overvoltage [30] and also as the proportionality factor smaller than unity which relates the logarithm of catalytic activity with the logarithm of the strength of the acid or base acting as a catalyst.

The series of negative ions $Br^-$, $OAc^-$, $OPh^-$, $OH^-$, which Ingold [5] finds to be increasingly active as substituting agents corresponding to their increasing " nucleophyllic strength " will be dealt by us as a series having increasing reaction heats, accompanied, according to the above theorem, by increasing reaction velocities.

*Chemistry Department,*
*University of Manchester.*

[30] This graphic presentation of the relation between reaction heat and activation energy by use of the relative inclination of the two potential curves at their crossing point is due to Dr. Horiuti who obtained the constant $\alpha$ of Tafel's equation in this manner.

# REVIEWS OF BOOKS.

**Magnetism and Matter.** By EDMUND C. STONER. (London : Methuen & Co., Ltd. Pp. xv + 575.

Dr. Stoner's treatise on *Magnetism and Atomic Structure* is well known to all workers in that field. But much has happened since 1926, the date of publication of that treatise, which was written before the development of the hypothesis of the spinning electron, and before the remarkable achievements of the quantum mechanics.

Many excellent treatises have been spoiled by ill-judged attempts to fit them for further service by hammering patches on their battered harness and, very wisely, Dr. Stoner has not attempted that almost impossible task. He has instead given us a new book, which is thoroughly up to date, while it yet preserves the historical perspective of the parent manual.

The scope of the book is wide, and the treatment, though the author does not shirk detail, is such that details are not permitted to obscure the broad outlines of the picture. After preliminary chapters dealing with earlier theories and results, with experimental methods and with the

quantum theory, the author proceeds to discuss the Zeeman and gyro-magnetic effects, the magnetic deviation of atomic rays, dia-, para-, and ferro-magnetism, investigations in strong fields, molecular magnetism and metal alloys. Very useful bibliographies are appended to each chapter.

That the volume is written by Dr. Stoner is sufficient guarantee of its accurate scholarship and philosophic breadth of view. It is quite indis-pensable to the specialist, and may be consulted profitably by all physicists interested in the development of modern atomic theories.

A. F.

**Ions, Electrons, and Ionising Radiations** (6th Edition). By Professor J. A. CROWTHER. (London : Arnold & Co., 1934. Pp. 340 + xi. 12s. 6d. net.)

The merit of this textbook is so well known that it is only necessary to indicate the nature of the changes made in the new edition. There have been many changes made in the text in order to bring into its scope the newer work on atomic physics and to make adjustments for the rapid change in physical theory since the last edition was written. This has meant the addition of two new chapters and also that several have been rewritten. The work is intended for students in the second year's course for a pass degree, and with this end in view the mathematical treatment has been simplified.

The story of the electrically charged particles that physics has brought to our ken is told with great simplicity and thoroughness and is, on this account, valuable not only as a textbook but also as a first book of refer-ence. It only lacks chapters on ionisation in solids and in solution to make it complete. But these are perhaps not regarded as within the scope of the subject which, although it is not indicated in the title, covers only those particles whose freedom to move in space is not hampered by van der Waal forces or by confinement in a solid lattice.

W. E. G.

**Relativity Physics.** By W. H. McCREA. Pp. vii + 87 (with 8 illus-trations). (London : Methuen & Co. Price 2s. 6d. net.)

The series of monographs, of which this is the latest member, has achieved a decided position in physical literature ; they provide the properly trained scientific reader, who may not be a specialist in any one field, with exactly the amount of information upon particular subjects which he needs. It must have been far from easy to do this in relativity theory, but Professor McCrea has managed it with an even touch which is really masterly. Since the treatment refers essentially to phenomena met with in the laboratory, the special theory suffices : the author is at pains to point out nevertheless the necessity of the generalised theory for astronomical purposes. The major part of the manual is concerned, naturally, with such matters as the Lorentz transformation, kinematics, optics and atomic physics, but in the last chapter we are given a brilliant little disquisition upon relativistic thermodynamics. As not infrequently happens, this branch of physics provides the most beautiful and subtle passages of all. In general, he who expends a modest half-crown upon this little volume will obtain good measure, pressed down and running over.

F. I. G. R.

**Richter-Anschütz Chemie der Kohlenstoffverbindungen oder Organische Chemie.** Zwölfte Auflage, Zweiter Band Erste Hälfte: Carbocyclische Verbindungen, Naturstoffe und Freie Organische Radikale, erste Hälfte, Alicyclische Verbindungen und Naturstoffe, bearbeitet von A. BUTENANDT, M. LIPP, K. NIEDERLÄNDER, F. REINDEL und F. ROCHUSSEN. (Leipzig: Akademische Verlagsgesellschaft m.b.H., 1935. Pp. 636. Price 38 marks paper; 40 marks bound.)

This volume of a new edition of a well-known treatise on organic chemistry deals with a number of topics which are of considerable interest at the present time. The first part is concerned with the cycloparaffins and their derivatives, the spirane compounds and the terpenes, including bicyclic terpenes, sesquiterpenes and polyterpenes. This includes a section on rubber in which the structure of the molecule and the question of polymerisation are briefly but clearly set out. The second half of the book deals with natural products arranged under the headings of glycosides (including nucleic acids), tannins, pepper constituents, natural dyestuffs (including, for example, the flavones and anthocyanins, hæmins and porphyrines, and chlorophyll), non-nitrogenous poisons (*e.g.*, hydnocarpic acid, pyrethrins, santonin, cantharadin and rotenone), the sterols and bile-acids, the vitamins and ascorbic acid, and the hormones (including thyroxin, insulin and the sexual hormones). It will be seen that the range of subjects touches physico-chemical interests at many points, and as a source of reliable and up-to-date information on the chemistry of these groups of substances the volume will certainly prove very useful. The style and method of treatment continues the Richter tradition of giving information without padding, with a judicious choice of references and handy tables.

J. R. PARTINGTON.

**Crystal Chemistry.** By O. HASSEL. Translated from the German by R. C. EVANS. Pp. xi + 94 (with 20 illustrations). (London: William Heinemann, Ltd. Price 6s.)

A notice of Dr. Hassel's book appeared in these *Transactions* about a year ago (**30**, 416, 1934), when a hope was expressed that an English version might one day appear. Unlike the majority of pious aspirations, this one has materialised, and that quickly. Dr. Evans has produced a satisfying translation, but he has also done a good deal more than that. In the first place, the original stood to gain by judicious expansion here and there; at the same time it was clear that certain aspects of the subject had escaped attention altogether. The former of these slight defects has been much reduced by the freedom of translation, and the latter by the inclusion of additional references and an appendix. Secondly, Dr. Evans is engaged in teaching the subject to Honours students, and this gives him a certain facility in presenting those features which experience shows to be stumbling blocks, with exceptional clarity.

The chemistry of the solid state has made a good beginning: it can scarcely be disputed that its study is unusually fascinating, and the translator may be well rewarded in the reflection that he will help many who "have not the German" to share in its beauties.

# THE RECOMBINATION OF HYDROGEN ATOMS.

By W. Steiner.

In a previous paper results have been given for measurements of the rate of recombination of hydrogen atoms by three-body-collisions.[1] The reaction constant was stated to be $k' = 9 \times 10^{15}$ cm.$^6$ sec.$^{-1}$ mole$^{-2}$, with an $H_2$ *molecule* as the third colliding particle, and to have at least $1/10$ of this value with an H *atom* as the third participant. The walls, poisoned by water vapour, appeared to have no obvious influence on the rate of recombination.

In the calculation of our results there was an error, as Amdur[2] pointed out. We should have taken a velocity varying with the composition of the reacting mixture of gases, instead of a constant velocity; this was too rough an approximation, as will become clear later on. Somewhat later, Amdur and Robinson[3] published results for the rate of recombination of H-atoms obtained by methods entirely different from ours and under different conditions. The average of their values for the highest pressure comes to $8\cdot5 \times 10^{15}$, which agrees remarkably well with our own measurements, considering the wide difference between the methods used. As the pressure decreases the constant increases, which means that there is a simultaneous wall-reaction. This constant is the same whether the third colliding particles are H-atoms or $H_2$ molecules and Amdur and Robinson consider that, if there were any difference for the two cases, it would be smaller ($k_{atom} : k_{molecule} \geqq 1 : 4$) than the one we gave. According to Amdur this discrepancy is accounted for by the above-mentioned error in calculation.

The fresh calculation we now give shows that the correction of our error has no considerable effect upon our former results. In particular, the difference between $H_2$ molecules and H atoms as third particle in recombination still holds. It can be shown that the results, as a whole, are satisfactorily described if the efficiency of the collisions in the case of atoms is $1/10$ of that for molecules. In agreement with Amdur and Robinson, we have also established the existence of some wall effect. Consequently, our new value for the constant $13 \times 10^{15}$ cm.$^6$ sec.$^{-1}$ mole$^{-2}$ now calculated must be considered as an *upper limit*. This value, however, must be a fairly close approximation, since the course of the reaction can be described in its essentials as a three-body reaction. In our new calculations we are at pains to prove fully the validity of the separate assumptions made.

[1] W. Steiner und F. W. Wicke, *Z. physik. Chem., Bodenstein Festband,* 1931, 817.

[2] I. Amdur, *Physic. Rev.,* 1933, **43**, 208.

[3] I. Amdur, and A. L. Robinson, *J. Amer. Chem. Soc.,* 1933, **55**, 1395.

22

Lastly, we have calculated the results on the assumption that the efficiency of an atom as third colliding particle is definitely greater than that of a molecule. This assumption was made in 1930 by Senftleben and Riechemeier and recently again by Smallwood,[4] to explain the results of their measurements. We shall see that it is entirely incompatible with our results.

## Experimental Results.

Before going into the calculations, we should explain how the experiments are carried out and how the numerical values on which the calculation is based are obtained from the measurements.

The hydrogen atoms were produced in the usual way in a Wood discharge tube. The mixture of molecules and atoms passed through the recombination tube, 250 cm. in length and of 2·5 cm. interior diameter. An *absolute* measurement was taken of the concentration of the hydrogen atoms at
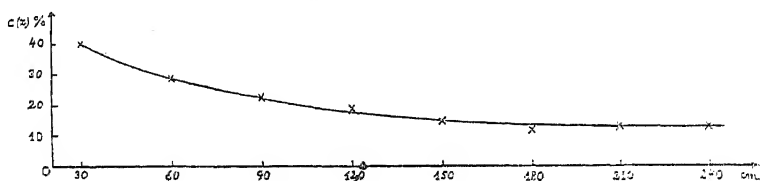


Experiment No. 1, $p = 0\cdot7$ mm., $u_z = 3\cdot85$ m./sec., $t = 20°$ C.
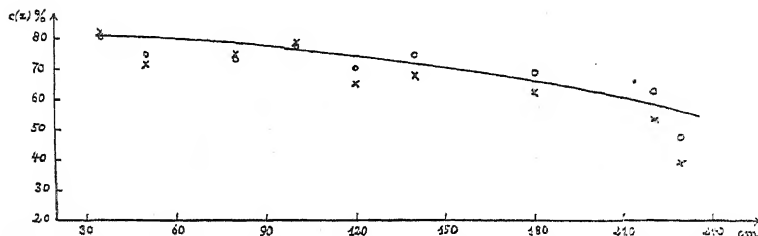


Experiment Nos. 5 and 6, $p = 0\cdot35$ mm., $u_z = 4\cdot00$ m./sec., $t = 20°$ C.

FIG. 1.

the entrance of the tube, using the Wrede slit method, then, at intervals of 30 cm. along the tube, *relative* measurements were taken by a spectroscopic method, calibrated from the first absolute determination. Thus the concentration of atoms was obtained as a function of the length $z$ of the recombination tube. Curves were drawn as smoothly as possible through the measured points, and from these curves were taken the atomic concentrations given in the following tables. The catalytic action of the walls was almost completely eliminated by poisoning through constant addition of 2·3 to 3·5 per cent. water vapour to the hydrogen gas. The decrease in pressure along the tube was nearly 10 per cent. from entrance to final measurement. This decrease, ignored in the earlier calculation, will be taken into account here. The velocity of flow $u_z$, which was supposed to be constant, was calculated by formula (11a), from the volume of gas per sec. pumped through the apparatus. The experiments were carried out at a temperature of 20° C.

[4] H. Senftleben and O. Reichemeier, *Ann. Physik*, 1930, (5), **6**, 105. H. M. Smallwood, *J. Amer. Chem. Soc.*, 1934, **56**, 1542.

## Calculation of the Experimental Results.

We introduce the following notations :—

Cylindrical co-ordinates :

$\begin{cases} z \text{ distance measured along the axis of the recombination tube.} \\ r \\ \phi \text{ angle round the axis in the plane vertical to the axis.} \end{cases}$

$2r_0$ diameter of the recombination tube.

$V_0$ volume of $H_2$ added or pumped off *per sec.*

$n_0$ number of moles of $H_2$ added or pumped off *per sec.*

$P$ exterior pressure in mm.

$p(z)$ pressure in mm. at the point $z$ of the recombination tube.

$t$ temperature in degrees Centigrade.

$N_L$ Loschmidt's number.

$N_{H_2}$ number of hydrogen molecules per $cm.^3$.

$N_H$ number of hydrogen atoms per $cm^3$.

Total concentration in $mole/cm^3$. :

$$N_L(N_H + N_{H_2}) = ([H] + [H_2]) = C \cdot p(z) \times 5 \cdot 5 \times 10^{-10} \quad . \quad (1)$$

Concentration of atoms in $mole/cm^3$. :

$$N_L N_H = [H] = c \cdot p(z) \times 5 \cdot 5 \times 10^{10} \qquad . \qquad . \quad (2)$$

Concentration of molecules in $mole/cm^3$. :

$$N_L N_{H_2} = [H_2] - (C - c) \cdot p(z) \times 5 \cdot 5 \times 10^{-10} \quad . \qquad . \quad (3)$$

In formulæ (1) to (3) $C$, $c$, $(C - c)$ are respectively the total, atomic and molecular concentrations as percentages of the total concentration at the point $z$; therefore $C = 100$. The factor $5 \cdot 5 \times 10^{-8}$ required in changing from moles to pressure, becomes $f = 5 \cdot 5 \times 10^{-10}$ when concentrations are expressed in percentages.

Relative concentration of atoms at the point $z$ :

$$\alpha' = \alpha'(z) = \frac{N_H}{N_H + N_{H_2}} - \frac{[H]}{[H] + [H_2]} = \frac{c}{C} = c \times 10^{-2} \quad . \quad (4)$$

$v_z$ linear velocity of flow in the direction of the axis

$D$ coefficient of diffusion.

$k_1$, $k_2$, $k_3$, $k_4$, and $k_5$: constants of the rate of the three-body reactions (compare p. 629).

## (a) Calculation of the Average Velocity of Flow $v_z$.

We calculate $v_z$ from the mole number $n_0$ of $H_2$ molecules (molecular weight $2M$) per sec. which enter the apparatus or come out of it. Mass will be transported through the tube-system of the apparatus

(a) by flow,
(b) by diffusion.

According to the equation of continuity, the *flow* per sec. per $cm.^2$ is given by $v_z \cdot \rho$

where $\qquad\qquad\qquad \rho = M[H] + 2M[H_2]$

hence $\qquad\qquad\quad v_z \cdot \rho = v_z M[H] + v_z 2M[H_2] \quad . \qquad . \qquad . \quad (5)$

direction of flow : $\qquad\quad$ atoms $\qquad\quad$ molecules
$\qquad\qquad\qquad\qquad\quad \longrightarrow \qquad\quad \longrightarrow$

The transport in the direction of $z$ by *diffusion* is given, in general, by

$$- D\frac{\partial \rho}{\partial z}$$

(diffusion to the wall, see p. 630).

If we denote by

$D'$ the coefficient of the diffusion of the atoms,
$D''$ the coefficient of the diffusion of the molecules,

Then for a mixture of gases of an average composition, the transport by diffusion becomes

$$- \left( D'M\frac{\partial [H]}{\partial z} + D''2M\frac{\partial [H_2]}{\partial z} \right).$$

Taking $([H] + [H_2])$ as being constant along the recombination tube to a first approximation (compensation of pressure), we have

$$\frac{\partial [H]}{\partial z} = - \frac{\partial [H_2]}{\partial z}$$

therefore the transport by diffusion is given by

$$- \left( D'\frac{\partial [H]}{\partial z}M - 2D''\frac{\partial [H]}{\partial z}M \right) = M\frac{\partial [H]}{\partial z}(2D'' - D') \qquad . \quad (6)$$

| Transport of atoms *in* the direction of flow. | Transport of molecules *opposite* to the direction of flow. |
|---|---|
| ⟶ | ⟵ |

The mass which enters the apparatus per sec. per cm.$^2$ is $\frac{2Mn_0}{r_0^2\pi}$. Therefore the *total* transport of mass per sec. per cm.$^2$ at the point $z$ is given by the general transport equation

$$Mv_z([H] + 2[H_2]) + M\frac{\partial [H]}{\partial z}(2D'' - D') = \frac{2Mn_0}{r_0^2\pi} \qquad . \quad (A)$$

or $\qquad v_z([H] + 2[H_2]) + \frac{\partial [H]}{\partial z}(2D'' - D') = \frac{2n_0}{r_0^2\pi} \qquad . \quad (A')$

The expression on the left-hand side of $(A')$ is *constant* in the stationary state, in which we make our observations; for inside the apparatus mass neither originates nor disappears. It may be seen from $(A)$ that the *flow* continuously transports mass, namely, atoms *and* molecules, in the direction from the discharge to the pump; this transport will be amplified by the *diffusion* of atoms, weakened, however, by the *rediffusion* of molecules. $\frac{\partial [H]}{\partial z}$ being always negative, it depends on the sign of $2D'' - D'$, if $2D'' < D'$ or $2D'' > D'$, whether the *total* transport by *diffusion* results in an amplification or in a weakening of the transport by *flow*.

According to Jeans,[5] $D'' = 1\cdot31$ cm.$^2$ sec.$^{-1}$ for hydrogen molecules at a pressure of 760 mm. Hg. Following his arguments we calculate $D'$ from the general formula $D = \epsilon\frac{\eta}{\rho}$.

[5] J. H. Jeans, *Dynamical Theory of Gases*, 4th ed., 1925, p. 322.

$\epsilon$ is an empirical factor of the mean value $1\cdot34 \times \rho$, the density is equal to $4\cdot5 \times 10^{-5}$ in the case of hydrogen atoms at atmospheric pressure. The viscosity $\eta$ for atomic hydrogen is, according to the measurements of Harteck,[6] $6\cdot9 \times 10^{-5}$. We have, therefore, $D = 2\cdot2$ cm.$^2$ sec.$^{-1}$. These values are valid for the diffusion of molecules into molecules or of atoms into atoms respectively. In our case we have a diffusion of molecules or atoms into a *mixture* of atoms and molecules ; here it is difficult to calculate the exact values, which depend on the composition of the mixture. For the same mixture we know only $2\cdot2 > D' > D''$, therefore $(2D'' - D') > 0$. The *total* diffusion re-transports mass and weakens the transport by flow.

This effect, however, is so small in all our experiments that we can neglect the diffusion completely in $(\mathbf{A}')$ as we shall see immediately from a rough estimation. We take experiments (Nos. 5 and 6 of Table IV.) at a low pressure where diffusion is most effective and calculate $v_z$ without taking into account diffusion to $6\cdot8 \times 10^2$ cm. $[H]+[H_2] = 1\cdot2 \times 10^2 . f$ ($f =$ factor for changing the units). We take the very ample value $(2D'' - D')$ at 760 mm. pressure to $0\cdot8$ ; then $(2D'' - D') = 1\cdot8 \times 10^3$ at $0\cdot35$ mm. ; $\frac{\partial[H]}{\partial z} = -10^{-1} \times f$. The transport by *diffusion* is $1\cdot8 \times 10^2 \times f$, the transport by *flow* $8\cdot2 \times 10^4 \times f$. The first is less than one-quarter per cent. of the transport by flow.

To calculate the average velocity of flow we use therefore the equation of transport $(\mathbf{A}'')$ which is simplified by neglecting diffusion

$$v_z([H] + 2[H_2]) = \frac{2n_0}{r_0^2\pi} \qquad . \qquad . \qquad . \qquad (\mathbf{A}'')$$

$[H]$ and $[H_2]$ may be determined from the measured concentration of atoms $\alpha'$ and the total pressure $p(z)$ at the point $z$ of the recombination tube.

$$\frac{[H]}{[H] + [H_2]} = \alpha' \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

$$[H] + [H_2] = b = \frac{p(z)}{RT} \qquad . \qquad . \qquad . \qquad (7)$$

therefore

$$[H] = \alpha'b \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (8)$$
$$[H_2] = (1 - \alpha')b \qquad . \qquad . \qquad . \qquad . \qquad (9)$$

and

$$v_z = \frac{n_0}{r_0^2\pi . b} \frac{2}{(2 - \alpha')} \qquad . \qquad . \qquad . \qquad (10)$$

$V_0$ is the volume of $H_2$ which enters the apparatus per sec. at the exterior pressure $P$, then

$$n_0 = \frac{V_0 P}{RT} \qquad . \qquad . \qquad . \qquad . \qquad (11)$$

Hence we have for $v_z$

$$v_z = \frac{V_0 P}{r_0^2\pi p(z)} \frac{2}{(2 - \alpha')} \qquad . \qquad . \qquad . \qquad (Ia)$$

[6] P. Harteck, *Z. physik. Chem.*, 1928, A **139**, 98.

At the entrance $z_1$ of the recombination tube we have for a gas which consists of molecules only ($\alpha' = 0$)

$$v_{z_1} = \frac{V_0 P}{r_0^2 \pi p(z_1)} \qquad . \qquad . \qquad . \qquad . \qquad (\mathrm{II}a)$$

FIG 2.

This value corresponds to the value $u_z = const.$ which we used in our former calculation. Introducing it in formula ($\mathrm{I}a$) we finally have

$$v_z = u_z \frac{p(z_1)}{p(z)} \frac{2}{(2 - \alpha')}. \qquad (\mathrm{I}b)$$

**(b) Calculation of the Velocity Constants.**

We consider a very small rectangular volume $d\Omega = dxdydz$ inside the recombination tube. There we have the following processes :

**1.** Recombination of atoms in a third body collision reaction

$$\left(\frac{\partial[\mathrm{H}]}{\partial t}\right)_z = -k_1[\mathrm{H}]^2([\mathrm{H}] + [\mathrm{H_2}]).$$

**2.** Flow of atoms coming from the discharge tube (we give the positive sign to the inward flow of atoms) (Fig. 2)

$$dxdy[\mathrm{H}]v_z - dxdy\left([\mathrm{H}] + \frac{\partial[\mathrm{H}]}{\partial z}dz\right)\left(v_z + \frac{dv_z}{\partial z}dz\right) = d\Omega\left(\frac{\partial[\mathrm{H}]}{\partial t}\right)_z$$

therefore we obtain

$$\left(\frac{\partial[\mathrm{H}]}{\partial t}\right)_z = -\left(v_z\frac{\partial[\mathrm{H}]}{\partial z} + [\mathrm{H}]\frac{\partial v_z}{\partial z}\right) = -\frac{\partial(v_z[\mathrm{H}])}{\partial z}.$$

**3.** Diffusion of atoms

$$\left(\frac{\partial[\mathrm{H}]}{\partial t}\right)_z = D \text{ div. grad. } [\mathrm{H}].$$

In the stationary state, we have for the sum of the three processes $\left(\frac{\partial[\mathrm{H}]}{\partial t}\right)_z = 0$. Hence the differential equation for the reaction becomes :

$$D \text{ div. grad. } [\mathrm{H}] - \frac{\partial(v_z[\mathrm{H}])}{\partial z} - k_1[\mathrm{H}]^2([\mathrm{H}] + [\mathrm{H_2}]) = 0. \quad . \quad (\mathrm{II})$$

To simplify this equation we neglect diffusion; we shall justify this assumption later and see how the results are to be modified by diffusion. Equation ($\mathrm{II}$) then becomes

$$-\left(v_z\frac{\partial[\mathrm{H}]}{\partial z} + [\mathrm{H}]\frac{\partial v_z}{\partial z}\right) - k_1[\mathrm{H}]^2([\mathrm{H}] + [\mathrm{H_2}]) = 0 \qquad . \qquad (\mathrm{III})$$

and for the constant $k_1$ we have

$$k_1 = -\frac{v_z\dfrac{\partial[\mathrm{H}]}{\partial z} + [\mathrm{H}]\dfrac{\partial v_z}{\partial z}}{[\mathrm{H}]^2([\mathrm{H}] + [\mathrm{H_2}])} \qquad . \qquad . \qquad . \qquad (\mathrm{IV})$$
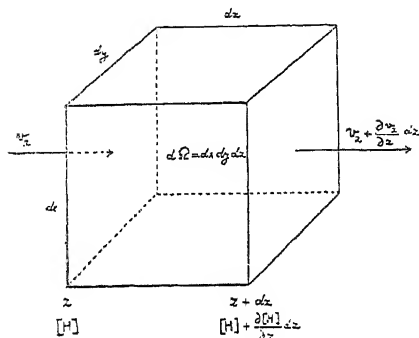
$k_1$ is valid for molecules *and* atoms as third colliding particles (on the assumption that $k_1 = k_{\text{atoms}} = k_{\text{molecules}}$).

We may define alternative constants as follows :

$k_2$ for *molecules* as third colliding particles $(k_\alpha = \tfrac{1}{10}k_m)$
$k_3$    ,,    ,,    ,,    ,,    $(k_\alpha \ll k_m)$
$k_4$ for *atoms* as third colliding particles $(k_\alpha \gg k_m)$
$k_5$    ,,    ,,    ,,    ,,    $(k_m = \tfrac{1}{20} k_\alpha)$.

We get these constants from (IV) by replacing the denominator $N_1$ by $N_i$ $(i = 2, \ldots 5)$. Therefore we have

$$k_i = k_1 \frac{N_1}{N_i} \qquad \qquad \qquad \qquad (12)$$

$$N_2 = [\text{H}]^2([\text{H}_2] + \tfrac{1}{10}[\text{H}])$$
$$N_3 = [\text{H}]^2[\text{H}_2]$$
$$N_4 = [\text{H}]^2[\text{H}]$$
$$N_5 = [\text{H}]^2([\text{H}] + \tfrac{1}{20}[\text{H}_2]).$$

For the general calculation we use only formula (IV), the other constants being easily obtained from equation (12). In (IV) we replace the molar by percentage concentrations. We have then

$$k_1 = - \frac{v_z \dfrac{\partial c}{\partial z} + c \dfrac{\partial v_z}{\partial z}}{c^2 C p(z)^2 (5 \cdot 5 \times 10^{-10})^2}.$$

We change the numerator

$$c = \alpha' \times 10^2 \qquad \frac{\partial c}{\partial z} = \frac{\partial \alpha'}{\partial z} \times 10^2$$

and according to (I*b*)

$$v_z = u_z \frac{p(z_1)}{p(z)} \frac{2}{(2 - \alpha')}$$

$$\frac{\partial v_z}{\partial z} = u_z p(z_1) \left\{ \frac{2}{2 - \alpha'} \frac{\partial}{\partial z} \frac{1}{p(z)} + \frac{1}{p(z)} \frac{\partial}{\partial z}\left(\frac{2}{2 - \alpha'}\right) \right\}$$

$$= u_z \frac{p(z_1)}{p(z)} \left\{ \frac{2}{(2 - \alpha')^2} \frac{\partial \alpha'}{\partial z} - \frac{2}{2 - \alpha'} \frac{1}{p(z)} \frac{\partial p(z)}{\partial z} \right\}$$

and it becomes

$$v_z \frac{\partial c}{\partial z} + c \frac{\partial v_z}{\partial z} = u_z \frac{p(z_1)}{p(z)} \frac{\partial c}{\partial z}\left\{ \frac{4}{(2 - \alpha')^2} - \frac{2}{(2 - \alpha')} \frac{c}{\partial c/\partial z} \cdot \frac{1}{p(z)} \frac{\partial p(z)}{\partial z} \right\}$$

therefore with

$$A = \left\{ \frac{4}{(2 - \alpha')^2} - \frac{2}{2 - \alpha'} \frac{c}{\partial c/\partial z} \cdot \frac{1}{p(z)} \frac{\partial p(z)}{\partial z} \right\} \qquad (13)$$

$$k_1 = - u_z \frac{p(z_1)}{p(z)} \frac{\partial c/\partial z \cdot A}{c^2 \cdot C \cdot p(z)^2 (5 \cdot 5 \times 10^{-10})^2}$$

multiplying the numerator and denominator by $p(z_1)^2$ we obtain

$$k_1 = \left[ - \frac{u_z \cdot \partial c/dz}{c^2 \cdot C \cdot p(z_1)^2 (5 \cdot 5 \times 10^{-10})^2} \right] . A . B \qquad (14)$$

where

$$B = \left(\frac{p(z_1)}{p(z)}\right)^3.$$

The fraction in brackets in (14) is none other than the constant $k$ which we calculated in our earlier paper using the constant velocity of flow $u_z$. Therefore we can write

$$k_1 = k \cdot A \cdot B \qquad . \qquad . \qquad . \qquad . \qquad (16)$$

To calculate the numerical values we substitute difference coefficients for the differential coefficients, then we have

$$A = \left\{ \frac{4}{(2 - \alpha')^2} - \frac{2}{(2 - \alpha')} \frac{c}{\Delta c / \Delta z} \cdot \frac{1}{p(z)} \frac{\Delta p(z)}{\Delta z} \right\}.$$

The second term of the equation does not change its sign, $\Delta c$ as well as $\Delta p(z)$ being negative. The average value of $\frac{1}{p(z)} \frac{\Delta p(z)}{\Delta z}$ is $4.8 \times 10^{-4}$ $\Delta z = 3 \times 10^1$; hence we obtain

$$A = \frac{4}{(2 - \alpha')^2} - \frac{2}{(2 - \alpha')} \frac{c}{\Delta c} \times 1.44 \times 10^{-2}$$

and

$$k_1 = - \frac{u_z \Delta c / \Delta z}{c^2 C p(z_1)^2 (5.5 \times 10^{-10})^2} A \cdot B. \qquad . \qquad . \qquad (17)$$

Tables I. to V. contain the values of $\Delta c$, $\Delta z$ and $z$, taken from our experimental curves, being the results of our measurements, the measured value of $u_z$, the old constant $k$, the necessary factors and finally the constants $k_1$, $k_2$, . . . $k_5$, for the different three-body collision reactions we considered in detail on page 629.

## (c) Influence of the Walls of the Recombination Tube.

To estimate the influence of the wall of the recombination tube we give another form to (II). Then the balance of the H-atom concentration for the stationary state inside the small volume $d\Omega$ becomes :

$$- \frac{\partial (v_z[H])}{\partial z} = k[H]^2([H] + [H_2]) - D \text{ div. grad. } [H] \quad . \quad (IIa)$$

surplus of the inward     consumption of atoms     consumption of atoms
flow of atoms     =     by reaction (homo-     +     by diffusion to the
geneous).     walls.

Equation (IIa) will be valid only if div. grad. [H] has a *negative* sign It is easily shown that this must always be the case.

In cylindrical co-ordinates we have :

$$\text{div. grad. } [H] = \frac{1}{r} \frac{\partial [H]}{\partial r} + \frac{\partial^2 [H]}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2 [H]}{\partial \phi^2} + \frac{\partial^2 [H]}{\partial z^2} \quad . \quad (18)$$

Assuming that the action of the walls is symmetrical round the axis of the tube we have $\frac{\partial^2 [H]}{\partial \phi^2} = 0$, furthermore $\frac{\partial^2 [H]}{\partial z^2}$ is very small compared to the other terms of equation (18) as we shall see later on from the experimental values (p. 635). With $\frac{\partial^2 [H]}{\partial z^2} = 0$ we obtain

$$\text{div. grad. } [H] = \frac{1}{r} \frac{\partial [H]}{\partial r} + \frac{\partial^2 [H]}{\partial r^2} \quad . \quad . \quad . \quad (19)$$

### Table I.—Experiment No. 1.—$p(z_1) = 0.7$ mm., $u_z = 3.85$ m/sec., $t = 20°$ C.

| $\Delta z$ | $\Delta c$ | $c = \alpha'.10^6$ | $c^2$ | $(C-c)$ | $k.10^{-15}$ | $\tfrac{2}{2-\alpha'}$ | $\tfrac{4}{(2-\alpha')^2}$ | $A$ | $B$ | $A.B$ | $k_1.10^{-15}$ | $k_2.10^{-15}$ | $k_3.10^{-15}$ | $k_4.10^{-15}$ | $k_5.10^{-15}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 30—60 | 40·0—30·0=10·0 | 35·0 | 1225 | 65·0 | 7·0 | 1·22 | 1·48 | 1·42 | 1·00 | 1·42 | 10·0 | 14·6 | 15·4 | 28·5 | 26·2 |
| 60—90 | 30·0—24·0=6·0 | 27·0 | 729 | 73·0 | 7·2 | 1·16 | 1·34 | 1·26 | 1·06 | 1·34 | 9·6 | 13·7 | 13·2 | 35·5 | 31·5 |
| 90—120 | 24·0—20·0=4·0 | 22·0 | 484 | 78·0 | 7·1 | 1·13 | 1·26 | 1·17 | 1·12 | 1·34 | 9·5 | 13·2 | 12·4 | 43·5 | 36·5 |
| 120—150 | 20·0—17·0=3·0 | 18·5 | 342 | 81·5 | 7·6 | 1·10 | 1·21 | 1·11 | 1·18 | 1·30 | 9·9 | 11·9 | 12·0 | 53·5 | 44·0 |
| 150—180 | 17·0—14·5=2·5 | 15·8 | 250 | 84·2 | 8·6 | 1·09 | 1·18 | 1·08 | 1·24 | 1·34 | 11·5 | 13·4 | 13·7 | 72·0 | 51·0 |
| 180—210 | 14·5—13·0=1·5 | 13·8 | 190 | 86·2 | 8·6 | 1·07 | 1·15 | 1·01 | 1·30 | 1·32 | 9·1 | 10·4 | 10·6 | 66·0 | 50·5 |
| 210—240 | 13·0—11·5=1·5 | 12·3 | 151 | 87·7 | 8·6 | 1·06 | 1·12 | 1·00 | 1·36 | 1·36 | 11·7 | 13·2 | 13·4 | 95·0 | 68·0 |

*average value :* $k_1 = 10\cdot2$, $k_2 = 12\cdot7$, $k_3 = 13\cdot0$

*maximum deviation from the average value :* $1\cdot5 = 14\cdot8\%$, $2\cdot3 = 18\%$, $2\cdot4 = 18\cdot5\%$

### Table II.—Experiment No. 2.—$p(z_1) = 0.55$ mm., $u_z = 4.00$ m/sec., $t = 20°$ C.

| $\Delta z$ | $\Delta c$ | $c = \alpha'.10^6$ | $c^2$ | $(C-c)$ | $k.10^{-15}$ | $\tfrac{2}{2-\alpha'}$ | $\tfrac{4}{(2-\alpha')^2}$ | $A$ | $B$ | $A.B$ | $k_1.10^{-15}$ | $k_2.10^{-15}$ | $k_3.10^{-15}$ | $k_4.10^{-15}$ | $k_5.10^{-15}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 30—60 | 59·0—51·0=8·0 | 55·0 | 3040 | 45·0 | 3·8 | 1·38 | 1·91 | 1·77 | 1·00 | 1·77 | 6·7 | 13·2 | 15·0 | 12·2 | 11·8 |
| 60—90 | 51·0—44·0=7·0 | 47·5 | 2260 | 52·5 | 4·5 | 1·32 | 1·73 | 1·69 | 1·06 | 1·79 | 7·6 | 13·2 | 14·2 | 16·0 | 15·2 |
| 90—120 | 44·0—38·0=6·0 | 41·0 | 1680 | 59·0 | 5·2 | 1·26 | 1·60 | 1·49 | 1·12 | 1·67 | 8·7 | 13·8 | 14·6 | 21·1 | 19·7 |
| 120—150 | 38·0—33·5=4·5 | 37·0 | 1370 | 63·0 | 4·8 | 1·23 | 1·51 | 1·27 | 1·18 | 1·50 | 7·7 | 13·6 | 14·0 | 20·8 | 19·2 |
| 150—180 | 33·5—30·0=3·5 | 31·7 | 1010 | 68·3 | 5·1 | 1·20 | 1·43 | 1·27 | 1·24 | 1·54 | 8·0 | 11·2 | 11·7 | 25·1 | 22·6 |
| 180—210 | 30·0—27·0=3·0 | 28·5 | 810 | 71·5 | 5·3 | 1·17 | 1·36 | 1·20 | 1·30 | 1·56 | 8·3 | 11·2 | 11·4 | 29·0 | 26·0 |
| 210—240 | 27·0—24·5=2·5 | 25·6 | 655 | 74·4 | 5·5 | 1·15 | 1·32 | 1·15 | 1·36 | 1·56 | 8·6 | 11·2 | 11·6 | 32·0 | 29·0 |

*average value :* $k_2 = 12\cdot1$, $k_3 = 13\cdot0$

*maximum deviation from the average value :* $1\cdot1 = 9\cdot1\%$, $2\cdot0 = 13\cdot4\%$

### Table III.—Experiment Nos. 3 and 4.—$p(z_1) = 0.35$ mm., $u_z = 4.00$ m/sec., $t = 20°$ C.

| $\Delta z$ | $\Delta c$ | $c = \alpha'.10^6$ | $c^2$ | $(C-c)$ | $k.10^{-15}$ | $\tfrac{2}{2-\alpha'}$ | $\tfrac{4}{(2-\alpha')^2}$ | $A$ | $B$ | $A.B$ | $k_1.10^{-15}$ | $k_2.10^{-15}$ | $k_3.10^{-15}$ | $k_4.10^{-15}$ | $k_5.10^{-15}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 30—60 | 48·0—44·5=3·5 | 46·2 | 2140 | 53·8 | 4·2 | 1·31 | 1·71 | 1·46 | 1·00 | 1·46 | 6·1 | 10·4 | 12·0 | 13·2 | 12·4 |
| 60—90 | 44·5—42·0=2·5 | 43·2 | 1870 | 56·8 | 4·3 | 1·28 | 1·64 | 1·32 | 1·06 | 1·40 | 6·1 | 10·0 | 10·8 | 14·2 | 13·2 |
| 90—120 | 42·0—39·0=3·0 | 40·5 | 1650 | 59·5 | 6·4 | 1·26 | 1·58 | 1·33 | 1·12 | 1·51 | 9·7 | 15·1 | 16·3 | 24·0 | 22·3 |
| 120—150 | 39·0—36·5=2·5 | 37·7 | 1420 | 62·3 | 5·7 | 1·23 | 1·52 | 1·24 | 1·18 | 1·48 | 8·4 | 12·8 | 12·3 | 22·2 | 20·5 |
| 150—180 | 36·5—34·0=2·5 | 35·2 | 1240 | 64·8 | 6·8 | 1·22 | 1·49 | 1·23 | 1·24 | 1·45 | 10·4 | 15·2 | 16·2 | 20·5 | 27·0 |
| 180—210 | 34·0—32·0=2·0 | 33·0 | 1090 | 67·0 | 6·6 | 1·20 | 1·45 | 1·17 | 1·30 | 1·52 | 10·0 | 14·2 | 14·7 | 30·3 | 27·5 |
| 210—240 | 32·0—30·2=1·8 | 31·0 | 961 | 69·0 | 6·8 | 1·19 | 1·42 | 1·12 | 1·36 | 1·52 | 10·4 | 14·5 | 14·6 | 32·0 | 30·0 |

*average value :* $k_2 = 13\cdot2$, $k_3 = 13\cdot8$

*maximum deviation from the average value :* $3\cdot2 = 24\cdot2\%$, $3\cdot0 = 22\%$

### Table IV.—Experiment Nos. 5 and 6.—$p(z_1) = 0.35$ mm., $u_z = 4.00$ m/sec., $t = 20°$ C.

| $\Delta z$ | $\Delta c$ | $c = \alpha'.10^6$ | $c^2$ | $(C-c)$ | $k.10^{-15}$ | $\tfrac{2}{2-\alpha'}$ | $\tfrac{4}{(2-\alpha')^2}$ | $A$ | $B$ | $A.B$ | $k_1.10^{-15}$ | $k_2.10^{-15}$ | $k_3.10^{-15}$ | $k_4.10^{-15}$ | $k_5.10^{-15}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 30—60 | 82·5—79·5=3·0 | 81·0 | 6560 | 19·0 | 1·9 | 1·67 | 2·78 | 2·13 | 1·00 | 2·13 | 4·0 | 14·8 | 20·0 | 5·4 | 4·9 |
| 60—90 | 79·5—76·0=3·5 | 77·7 | 6037 | 22·3 | 2·3 | 1·64 | 2·70 | 2·18 | 1·06 | 2·30 | 5·3 | 17·8 | 23·5 | 6·8 | 5·8 |
| 90—120 | 76·0—73·0=3·0 | 74·5 | 5550 | 25·5 | 2·1 | 1·60 | 2·56 | 2·00 | 1·12 | 2·24 | 4·7 | 14·0 | 18·4 | 6·3 | 6·1 |
| 120—150 | 73·0—69·0=4·0 | 71·0 | 5041 | 29·0 | 3·1 | 1·54 | 2·38 | 1·98 | 1·18 | 2·34 | 7·3 | 20·0 | 26·5 | 10·2 | 10·0 |
| 150—180 | 69·0—65·0=4·0 | 67·0 | 4489 | 33·0 | 3·5 | 1·51 | 2·27 | 1·90 | 1·24 | 2·35 | 8·2 | 20·5 | 25·8 | 12·2 | 11·9 |
| 180—210 | 65·0—61·0=4·0 | 63·0 | 3969 | 37·0 | 4·0 | 1·47 | 2·14 | 1·80 | 1·30 | 2·30 | 9·2 | 21·0 | 25·0 | 14·4 | 14·2 |

*average value :* $k_2 = 18\cdot0$, $k_3 = 23\cdot2$

*maximum deviation from the average value :* $4\cdot0 = 22\cdot2\%$, $4\cdot8 = 20\cdot7\%$

### Table V.—Experiment Nos. 7 and 8.—$p(z_1) = 0.35$ mm., $u_z = 3.75$ m/sec., $t = 20°$ C.

| $\Delta z$ | $\Delta c$ | $c = \alpha'.10^6$ | $c^2$ | $(C-c)$ | $k.10^{-15}$ | $\tfrac{2}{2-\alpha'}$ | $\tfrac{4}{(2-\alpha')^2}$ | $A$ | $B$ | $A.B$ | $k_1.10^{-15}$ | $k_2.10^{-15}$ | $k_3.10^{-15}$ | $k_4.10^{-15}$ | $k_5.10^{-15}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 30—60 | 77·0—72·5=4·5 | 74·7 | 5600 | 25·3 | 2·3 | 1·60 | 2·56 | 2·18 | 1·00 | 2·18 | 5·0 | 15·2 | 19·8 | 6·9 | 6·7 |
| 60—90 | 72·5—68·5=3·5 | 70·5 | 4980 | 29·5 | 2·4 | 1·54 | 2·38 | 1·99 | 1·06 | 2·10 | 5·0 | 13·6 | 16·8 | 7·1 | 7·0 |
| 90—120 | 68·5—64·5=4·5 | 66·2 | 4410 | 33·8 | 4·0 | 1·49 | 2·24 | 1·92 | 1·12 | 2·15 | 8·6 | 20·0 | 22·5 | 12·9 | 12·6 |
| 120—150 | 64·5—60·0=4·0 | 62·0 | 3850 | 38·0 | 3·3 | 1·45 | 2·10 | 1·78 | 1·18 | 2·10 | 6·9 | 15·8 | 18·0 | 11·1 | 10·8 |
| 150—180 | 60·0—56·0=4·0 | 58·0 | 3370 | 42·0 | 3·7 | 1·42 | 2·00 | 1·69 | 1·24 | 2·10 | 7·8 | 16·4 | 18·4 | 12·6 | 13·0 |
| 180—210 | 56·0—52·0=4·0 | 54·0 | 2926 | 46·0 | 4·6 | 1·37 | 1·88 | 1·61 | 1·30 | 2·10 | 9·7 | 18·8 | 21·0 | 17·9 | 17·4 |

*average value :* $k_2 = 16\cdot6$, $k_3 = 19\cdot4$

*maximum deviation from the average value :* $3\cdot4 = 20\cdot5\%$, $3\cdot1 = 16\%$

In general the sign of this expression can be positive *or* negative. We have, indeed, constantly $\dfrac{\partial[H]}{\partial r} < 0$ but $\dfrac{\partial^2[H]}{\partial r^2} \begin{cases} < 0 \\ \text{or} \\ > 0 \end{cases}$ therefore the sign of (19) depends on the shape of $[H(r)]$. The general shape of $[H(r)]$ in our case may be seen from Fig. 3, but we cannot decide the sign of div. grad. [H] without knowing the exact value of $[H(r)]$.

But we have to remember that we do not actually measure the value $[H(r, z)]$. What we really measure, with the slit method and especially with the spectroscopic method, is a mean-value taken over the cross-section of the tube
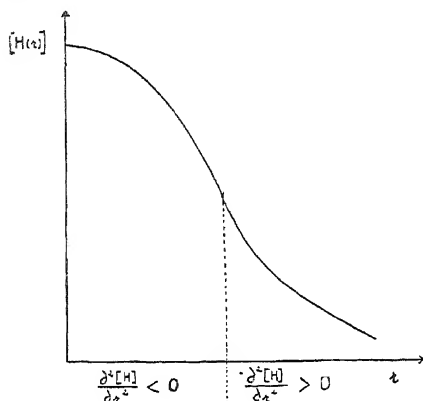


$$[H(z)] = \frac{1}{r_0}\int_0^{r_0}[H(r, z)]dr.$$

FIG. 3.

Therefore we have also to replace in (IIa) div. grad. [H] by an average value, which is given by

$$\overline{\text{div. grad. }[H]} = \frac{1}{r_0}\int_0^{r_0}\text{div. grad. }[H]dr = \frac{1}{r_0}\int_0^{r_0}\frac{1}{r}\frac{\partial[H]}{\partial r}dr + \frac{1}{r_0}\int_0^{r_0}\frac{\partial^2 H}{\partial r^2}dr. \quad (20)$$

It is easy to show that (20) must be *negative*, quite independently of the special shape of $[H(r)]$.

We notice first that at the axis of the tube, $r = 0$, $[H(r)]$ must have its maximum value, therefore

$$\left(\frac{\partial[H]}{\partial r}\right)_{r=0} = 0.$$

Next we consider the first integral in (20)

$$\frac{\partial[H]}{\partial r} < 0 \text{ in the whole interval, except for } r = 0,$$

therefore

$$\frac{1}{r}\frac{\partial[H]}{\partial r} < 0 \text{ in the whole interval, except for } r = 0$$

$$\left(\frac{1}{r}\frac{\partial[H]}{\partial r}\right)_{r=0} = 0$$

as sum of all these products the first integral is negative.

$$\frac{1}{r_0}\int_0^{r_0}\frac{\partial^2[H]}{\partial r^2}dr = \frac{1}{r_0}\left\{\left(\frac{\partial[H]}{\partial r}\right)_{r=r_0} - \left(\frac{\partial[H]}{\partial r}\right)_{r=0}\right\}.$$

This integral must be also negative, if we remember the assumptions made concerning $\dfrac{\partial[H]}{\partial r}$. Hence we obtain

$$\overline{\text{div. grad. }[H]} < 0.$$

We have then

$$k = -\frac{\partial(v_z[H]/\partial z}{[H]^2([H] + [H_2])} + \frac{D^*}{p}\frac{\overline{\text{div. grad. }[H]}}{[H]^2([H] + [H_2])}. \quad (21)$$

If we replace $D$ by $D^*/p$ ($D^*$ is the coefficient of diffusion at 1 mm. pressure for a mixture of gases of known composition). We denote the whole expression (21) by $k_{theor.}$ and its first term by $k_{exp.}$ in accordance with (IV).

$$k_{theor.} = k_{exp.} - \frac{D^*}{p} \frac{|\overline{\text{div. grad. [H]}}|}{[H]^2([H] + [H_2])}. \qquad . \qquad . \qquad (22)$$

This equation makes it evident how $k_{exp.}$ is affected by a wall-reaction. Calculated according to (22) it will increase, if the total pressure $p$ decreases. We get, therefore, the *right* value $k_{theor.}$ of the three-body collision reaction if we subtract from $k_{exp.}$ a quantity as given by the second term of (22).

## Discussion of the Results.

Consider the calculated constants $k_1, k_2, \ldots k_5$. It is evident that the values for $k_4$ and $k_5$ are not constant; at all pressures they have a considerable drift—up to three times the initial value. The drift is not very different whether we take $k_\alpha \gg k_m$ ($k_4$) or $k_m = \frac{1}{20}k_\alpha$ ($k_5$). Therefore it is in no way consistent with our results that the hydrogen *atom* as third colliding particle should be more effective in the recombination reaction than the hydrogen molecule.

The *constant* $k_1$ ($k_m = k_\alpha$) gives a very satisfactory value at the highest pressure and at the smallest relative concentration of atoms. At smaller pressures, however, whilst increasing to twice the initial value in the course of one experiment, it decreases if we go from one experiment to another one at a lower pressure. This decrease of the constant with decreasing pressure is in no way understandable. We should expect the opposite : that a wall reaction would be appreciable and would *increase* the constant. Therefore we conclude that the assumption of *equal* efficiency of atoms and molecules as third colliding particles is also not compatible with our experimental results.

Lastly we have to consider the constants $k_2$ and $k_3$. Sometimes they have also a small drift but they give the best representation of the whole of our experiments. Constants $k_2$ and $k_3$ being the reaction constants for molecules as third colliding particles (p. 629) we denote them by $k_m'$ and $k_m$ respectively. To give a better survey we have put together in Table VI. the average values of $k_m'$ and $k_m$ at different pressures.

TABLE VI.

| | $p$ (mm.). | $k_m' \times 10^{-15}$. | $k_m \times 10^{-15}$. |
|---|---|---|---|
| 1 | 0·7 | 12·7 ± 2·3 | 13·0 ± 2·4 |
| 2 | 0·55 | 12·1 ± 1·1 | 13·0 ± 2·0 |
| 3 | 0·35 (small concentration of atoms) | 13·2 ± 3·2 | 13·8 ± 3·0 |
| 4 and 5 | 0·35 (great concentration of atoms) | 17·3 ± 3·7 | 21·3 ± 3·9 |
| Increase of the constant with decreasing pressure | | 36 per cent. | 64 per cent. |

We give there also the *maximum* deviation from the average value in order not to overestimate the exactness of our results.

Both constants increase with decreasing pressure. In addition to the homogeneous three-body collision reaction we have, therefore, a wall reaction, which is evidently not completely suppressed by poisoning the walls with water vapour. This explains why the experiments were not so remarkably reproducible at low pressures as at the highest pressure. For it is very probable that the recombining action of the wall may not be constant along the whole length of the tube, and may differ from one experiment to another. So, for instance, the influence of the wall seems to be rather small in Nos. 3 and 4 of Table III. as compared with the other experiments. By chance the wall may have been poisoned very thoroughly in that experiment.

Since we can represent the whole experimental results with the same exactness either by $k_m'$ or by $k_m$, we cannot decide between these two possibilities. We therefore make the two following assumptions for our reactions :

**1.** Small wall reaction and $k_\alpha = \frac{1}{10} k_m'$

or

**2.** Greater wall reaction and $k_\alpha = 0$.

For the absolute values of the constants $k_m'$ and $k_m$ we can give only an *upper* limit, namely, the values at the highest pressures :

$$k_m' < 12\cdot7 \times 10^{15} \text{ cm.}^6 \text{ sec.}^{-1} \text{ mole}^{-2}$$
$$k_m < 13\cdot0 \times 10^{15} \text{ cm.}^6 \text{ sec.}^{-1} \text{ mole.}^{-2}.$$

These are practically the same.

They are enlarged by the *wall reaction*. Were it possible to calculate its magnitude we should get the exact homogeneous reaction constants. Unfortunately we have to content ourselves with a very rough approximation. Consider equation (22)

$$k_{\text{theor.}} = k_{\text{exp.}} - \frac{D^*}{p} \frac{|\overline{\text{div. grad. }[H]}|}{[H]^2([H] + [H_2])} \quad . \quad . \quad . \quad (22)$$

where

$$\frac{D^*}{p} \frac{|\overline{\text{div. grad. }[H]}|}{[H]^2([H] + [H_2])} = \frac{D^*}{p} \frac{\left| \frac{1}{r_0} \left\{ \int_0^{r_0} \frac{1}{r} \frac{\partial[H]}{\partial r} dr + \left( \frac{\partial[H]}{\partial r} \right)_r \right\} \right|}{[H]^2([H] + [H_2])} \quad (23)$$

gives the influence of the wall. It is impossible to calculate the numerator of (23) since we do not know $\frac{\partial[H]}{\partial r}$. We have therefore two unknown values in (22), $k_{\text{theor.}}$ and $a$ defined by

$$D^* |\overline{\text{div. grad. }[H]}| = D^* |\overline{\text{div. grad. }c}| \, p(z) \, . f = ap(z) \, . f.$$

If we assume that in all our experiments the wall has the same recombining action, which assumption is not valid in all cases as mentioned above (compare experiments Nos. 3 and 4 with the others), we can calculate $a$ and $k_{\text{theor.}}$ from two experiments at different pressures. It seems plausible to replace $a$ by $\frac{2}{3}a$, for the *smaller* atom-concentrations, since we may then expect $\frac{\partial[H]}{\partial r}$ and $D^*$ to be on the average smaller.

We should like to emphasise that because of the rough estimation made we do not claim that the probable values given for $k_m'$ and $k_m$

## TABLE VII.

| Calculated from | $a.$ | $k_m' \times 10^{-15}.$ | $a.$ | $k_m \times 10^{-15}.$ |
|---|---|---|---|---|
| Exp. No. 1 and No. 7 + 8 . | 11·5 | 11·8 | 13·0 | 11·9 |
| Exp. No. 2 and No. 7 + 8 . | 14·8 | 10·5 | 15·0 | 11·2 |
| Average probable values . . | 13·0 | 11·2 | 14·0 | 11·6 |

(In calculating the values $a$, $k_m'$ and $a$, $k_m$ of the table the denominator $[H]^2([H] + [H_2]) = N_1$ has been replaced by $N_2$ and $N_3$ respectively.)

are exact. We have made this estimate to show that the upper limit given cannot differ very much from the right values. This is only an alternative statement of the fact that we have been able to represent our measurements ⸂as a homogeneous three-body collision reaction. To get the exact values we should have to carry out experiments at much higher pressures.

Finally we can now estimate the order of magnitude of the different terms in the equation

$$-\frac{\partial(v_z[H])}{\partial z} = k_m'[H]^2([H] + \tfrac{1}{10}[H_2])$$
$$- D\frac{1}{r_0}\left\{\int_0^{r_0} \frac{1}{r}\frac{\partial[H]}{\partial r}dr + \left(\frac{\partial[H]}{\partial r}\right)_{r_0}\right\} - D\frac{\partial^2[H]}{\partial z^2}.$$

We have for instance :—

For experiment No. 5 + 6 :
($p = $ 0·35 mm.)
$$120 \quad = \quad 84·8 \quad + \quad 37 \quad - \quad 1·8$$
and experiment No. 1 :
($p = $ 0·7 mm.)
$$215 \quad = \quad 194·9 \quad + \quad 12·3 \quad + \quad 7·8$$

We see immediately that we can neglect the term giving the diffusion along the tube at both pressures, since it is very small compared with the other terms. Our approximation $D\frac{\partial^2[H]}{\partial z^2} = 0$, made on page 630 is therefore justified.

The wall reaction is nearly 30 per cent. of the whole reaction at low pressure and goes back to nearly 5 per cent. at the higher pressure. These values are also only a rough estimation.

The new calculation confirms our old results. Therefore the discrepancy between our results and those of Amdur and Robinson still exists. It arises, we believe, from the use of the calorimeter method by these authors. We have carried out experiments to compare the two absolute methods for measuring the concentration of atoms, *viz.*, the Wrede slit method and the calorimeter method. These experiments, together with an extension of the calculations given above, will be published shortly and will show the influence of diffusion on the calorimeter method and the precautions which must be taken to avoid errors in measuring atom-concentrations.

## Summary.

Results for the rate of recombination of hydrogen atoms given in a previous paper are corrected by means of a new precise calculation taking into account the effect of diffusion. It is found that in addition to the homogeneous three-body-collision reaction there is a small wall reaction. Therefore we can deduce only an *upper limit* for the recombination constant $k_m < 13 \cdot 0 \pm 2 \cdot 0 \times 10^{15}$ cm.$^6$ sec.$^{-1}$ mole$^{-2}$ at 20° C. for a *molecule* as third colliding particle. This value is $1/10$ or less when an *atom* is the third colliding particle. According to a rough estimate the real value is nearly $k_m = 11 \cdot 0 \pm 2 \cdot 0 \times 10^{15}$ cm.$^6$ sec.$^{-1}$ mole$^{-2}$ at 20° C.

# ANODIC PASSIVATION.

By W. J. Shutt.

In a recent number of this Journal[1] Armstrong and Butler describe measurements of the limiting current densities at which gold plates may dissolve anodically in unstirred solutions of chlorides. They also determined the time effect associated with the appearance of passivity for currents beyond these limiting values, and derived a relation between current density and time required for passivation similar to that found by Shutt and Walton.[2] Using both their own figures and some of those obtained by Shutt and Walton, they have calculated, in two different ways, the thickness of the diffusion layers in contact with the anode. They assume that such layers must always exist for any practicable degree of agitation of the electrolyte. The figures they obtain are consistent and of reasonable dimensions for such diffusion layers. They finally conclude however that the whole of our results may be explained in terms of diffusion and therefore are probably not in any sense a measure of the ultimate passivating process even though the latter may still proceed through some such mechanism as that which we have utilised in our work.

In view of this conclusion it seems desirable that some account should be given of the main reasons which finally induced Shutt and Walton to abandon all idea of the existence of any appreciable diffusion layer under the conditions employed in the majority of their experiments.

It was observed that only at high current densities (and therefore short times of passivation) was the relation $T(C - C_0) = K$ valid for all rates of stirring. In this expression $T$ represents the time in seconds required for passivation, $C$ the current density, $C_0$ a constant, and $K$ a constant having the dimensions of coulombs.[2] With continuous increase in the rate of flow of electrolyte over the anode surface,

[1] Armstrong and Butler, *Trans. Faraday Soc.*, 1934, **30**, 1173.
[2] Shutt and Walton, *Trans. Faraday Soc.*, 1934, **30**, 914.

this expression became applicable to longer times of passivation until finally a short extrapolation to $T = \infty$ of the straight line representing $1/T$ against $C$ showed that $C_0$ could be identified with the limiting maximum current density at which gold would dissolve in the particular chloride solution under investigation. This limiting current was determined, for the same rate of stirring, by direct observation of the ampèrage beyond which a very small increase sufficed for a sudden change of the electrode process from solution of gold to evolution of chlorine. Beyond the limiting degree of agitation of the solution, further increase in rate of flow of electrolyte caused no apparent change in time of passivation for any fixed current density. This fact was taken to indicate either that a lower limit to the possible thickness of the diffusion layer had been reached, or that the diffusion layer had been eliminated altogether.

A further objection to the diffusion hypothesis arose in the interpretation of data obtained from experiments on the anodic passivation of iron in sulphate solutions. Publication of this work has been delayed through the complications which arise when working with iron. The sensitivity of the metal to impurities and heat and mechanical treatment render it almost impossible to rely on the reproducibility of the surface. This difficulty has been minimised by preparing electrolytic sheet and annealing *in vacuo*. Other difficulties arise from the relatively high reactivity of the active metal; in air, or neutral or alkaline electrolytes it spontaneously assumes a film of oxide; and hydrogen, which acts as a depolariser on the subsequent application of current, is readily absorbed by the surface layers of the metal.[3] Measurements have been possible, however, under certain conditions and the results show a close analogy with those for the passivation of gold in chlorides. For instance, in well stirred, $1 \cdot 0 N$, $H_2SO_4$ at $25°$, the relation $T(C - C_0) = K$ was found to hold, $C_0$ was $1 \cdot 22$ amp./cm.[2] and $K$ was $0 \cdot 58$ coulombs per cm.[2] of surface of iron. In this case it is difficult to conceive of a reaction analogous to the formation of $AuCl_4^-$ to account for the removal of anion from the diffusion layer. In fact, if a diffusion layer exists, the concentration within it can only increase until passivation sets in.

In view of the objections which arose against any theory based on diffusion in the electrolyte, it seemed wiser to assume that the vigorous stirring had reduced the diffusion layer to molecular dimensions and that the figures obtained under such conditions were actually a measure of the rate of formation of the adsorption film.

The objection raised by Armstrong and Butler that some of our values of $K$ are so large as to represent many molecular layers of adsorbed ions, does not arise, since we do not consider that the adsorbed layer of chloride is a static system in the same sense as is the oxide film finally formed. The ions might be supposed to have only a short life in the adsorbed state but, in the absence of current, a dynamic equilibrium is rapidly established. On passage of the current, the available ions are discharged and the subsequent reactions depend on the nature of those ions.

[3] Shutt and Walton, *Trans. Faraday Soc.*, 1933, **29**, 1209.

# THE DISSOLUTION OF MAGNESIUM IN AQUEOUS SALT SOLUTIONS. PART IV.

## By L. Whitby.

In previous communications [1] dissolution experiments were described with magnesium the surface of which was free from visible films. The invisible oxide film on metals frequently determines the course of subsequent wet corrosion, but little work has been done, and none, apparently, with magnesium, on the effect of visible air-formed films.

Magnesium in moist atmospheres rapidly becomes coated with corrosion product that exhibits, in general, no protective action; [2] Pilling and [3] Bedworth showed that the oxide film formed on magnesium at high temperatures is also non-protective. Such films are not necessarily non-protective against solutions containing comparatively large, solvated ions; chemical action of the liquid may, however, cause the removal of air-formed films.

Dissolution/time curves, up to 24 hours, have now been obtained at $25°$, in $N$, $0·01N$ and $0·001N$ solutions of both sodium chloride and sodium sulphate, using magnesium specimens that were previously exposed, after cleaning, to an indoor atmosphere for either 30 minutes, 2 hours, 17 hours, or 21 days. The specimens exposed for 21 days were covered with an apparently uniform, greyish-white, film; the remainder appeared unchanged. The two shortest exposures were made in the corrosion vessels; the longest in a room free from laboratory fumes. Published analyses of corrosion product obtained from magnesium exposed for 300, or more, days in the above-mentioned room, show that most of the product consists of hydrated magnesium carbonate together with smaller amounts of sulphate and hydroxide. [2] Magnesium hydroxide was probably first formed and hence it is assumed that the product on the present specimens consisted mainly of that compound.

The relative humidity was shown to control the rate of attack and the existence was demonstrated of a critical humidity above which the weight-increments showed large increases. [2] Approximately equal weight-increments were obtained on specimens exposed during different periods, by ensuring that the relative humidities remained, if not constant, at least below the critical figure. Readings consequently were taken daily by means of a wet and dry bulb thermometer; all specimens used were exposed to relative humidities not exceeding 75 per cent. Experiments were performed at least in duplicate and 4 or 6 were made when reproducibility was not satisfactory.

Magnesium foil, MgUR, was used, specimens being $1 \times 4$ cm. with a punched hole for suspension; the analysis has been given previously, [1(c)] also the method of preparation of the surface, together with experimental procedure. [1(a)]

Results are illustrated in Figs. 1-4 and points shown on the curves each represent the mean of the number of experiments performed.

[1] Whitby, *Trans. Faraday Soc.*, 1933, **29**, (*a*) 415, (*b*) 523, (*c*) 853, (*d*) 1318.
[2] *Ibid.*, 844.  [3] *J. Inst. Metals*, 1923, **29**, 577.

The curves show that the air-formed film was protective neither in sulphate nor in chloride solutions. The presence of the film, produced by



Hours
Minutes
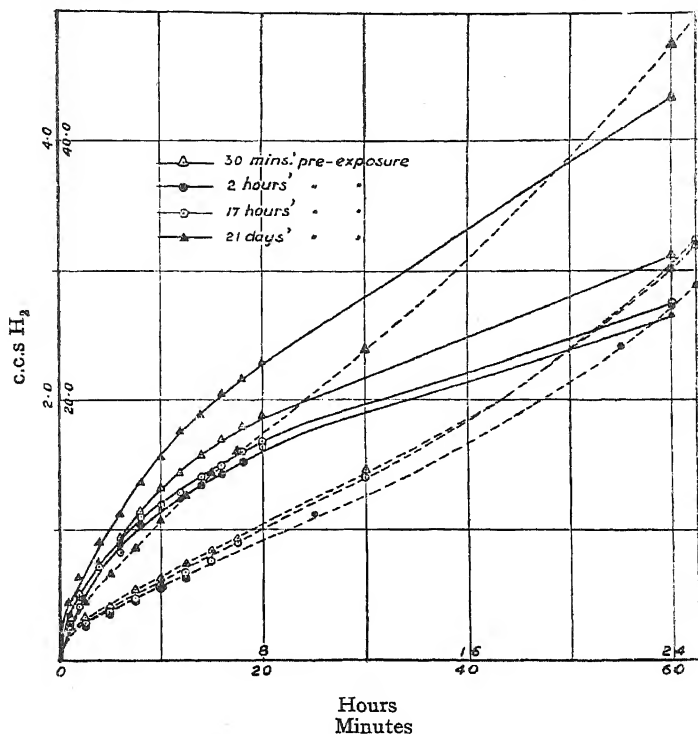
FIG. 1.—*N* sodium chloride.   Broken curves are later stages.



Hours
Minutes
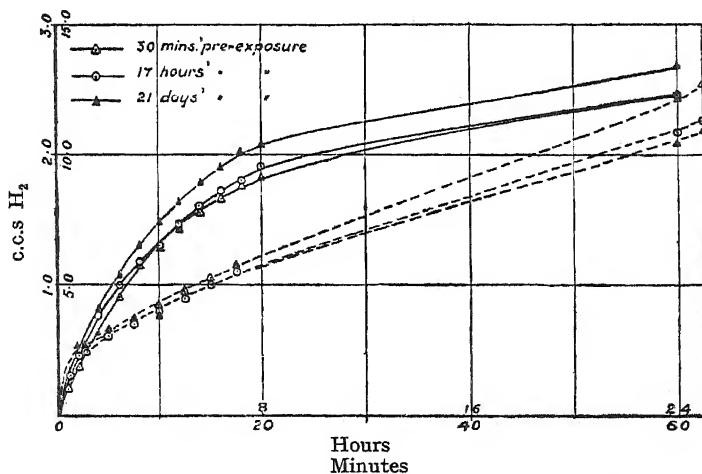
FIG. 2.—*N* sodium sulphate.   Broken curves are later stages.

3 weeks' exposure, sometimes caused an increased rate of attack, which was evident even from the initial stages of the reaction.   The increase

was more marked in $N$ sodium chloride (Fig. 1) than in $N$ sodium sulphate (Fig. 2) which gave nearly identical curves, with variations little more than those normal between duplicates.    The differences in rates of dissolution in $N$ sodium chloride, shown by specimens subjected to short periods of pre-exposure, are not sufficiently marked for comment.    An
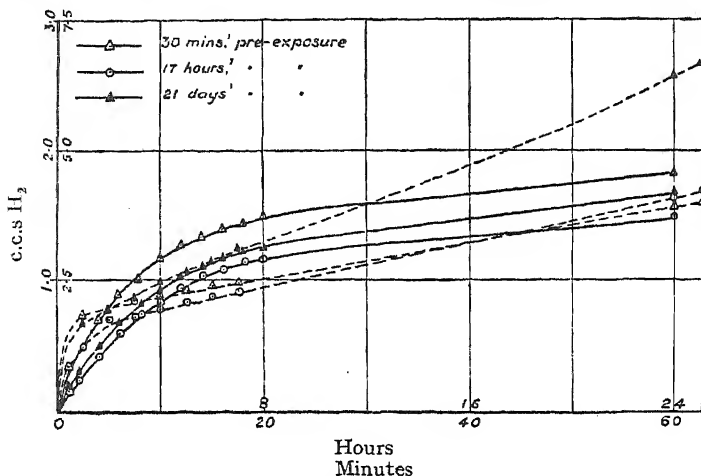


FIG. 3.—0·01 $N$ sodium chloride.    Broken curves are later stages.

increased rate of attack on the specimens pre-exposed for 3 weeks was caused by both sodium chloride and sodium sulphate solutions of 0·01$N$. The increase became marked, however, only during the later stages of the dissolution ; again no protective effect was observed.    The curves for 0·001$N$ solutions are omitted for the sake of brevity, but chloride solution
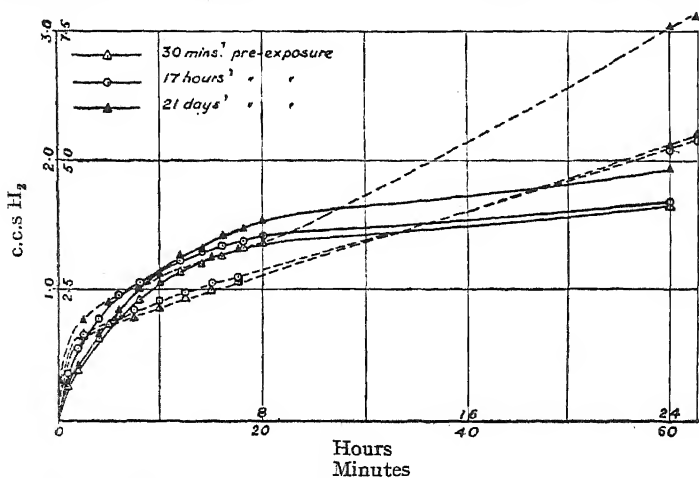


FIG. 4.—0·01 $N$ sodium sulphate.    Broken curves are later stages.

gave results similar to those obtained in 0·01$N$ solution whereas sulphate solution gave almost identical results with all the specimens.    The increased rate of attack caused by the thick films may have resulted from the porosity of the film coupled with the ability of the particles to act as cathodes.    Experimental evidence [1] [d] shows that corroding magnesium

is usually under anodic control, whereas the suggestion of increased attack caused by the cathodic nature of the air-formed film presupposes cathodic control under certain conditions. The acceleration of the rate of attack of corroding magnesium caused by redeposition of traces of certain metallic impurities,[4a, b] must receive a similar explanation. Evans and Hoar [4a] suggest a mixed control (*sic*) for magnesium but experimental evidence indicates that under normal conditions the control is anodic ; cathodic control may supervene, however, when conditions are such that the cathodic polarisation (potential/current) curve is moved bodily in the necessary direction.[4a] Such conditions may include the formation of porous metallic or non-metallic coatings, cathodic to magnesium and of lower hydrogen overpotentials. An analogous case is recorded by Britton, Hoare and Evans,[5] who show that iron, normally under cathodic control in chloride solutions, may change to anodic control after addition of soluble sulphides to the solution. They state that " the anodic polarisation curve is shifted bodily. . . ."

It is shown later (Table II.) that the solubility of magnesium hydroxide is considerably higher in solutions of sodium sulphate than in those of sodium chloride. It is probable, therefore, that most of the air-formed film was dissolved in the $N$ sulphate solutions. Hence, the reason becomes apparent for increased attack in $N$ sodium chloride, but not in $N$ sodium sulphate, of the specimens pre-exposed for 3 weeks. The solubility of magnesium hydroxide is probably lower and nearly the same in both chloride and sulphate solutions of greater dilution, such as $0.01N$, and the relative behaviours of the hydroxide-coated specimens in either solution should be approximately the same ; Figs. 3 and 4 confirm this.

## Effect of Concentration of Salt Solutions.

The effect of concentration of sodium chloride solutions on the rate of dissolution of magnesium therein has been investigated previously by Hughes [6] and by Endo and Miyasaki,[7] but no account was taken of the influence of traces of metallic impurities in the metal nor of the effect of time on the reaction rates. Hughes used magnesium powder of doubtful composition and coated with corrosion product ; neither gave complete analyses of the metal. In spite, however, of the probable differences of composition of the metal used, in both cases maxima of the rate of dissolution were obtained in solutions of concentration between 1 and 2 $N$. Hughes ascribed the maximum to " a specific effect of the dissolved sodium chloride on the water," but Endo and Miyasaki stated that it corresponded to a maximum in the magnesium hydroxide solubility curve.

Experiments have now been completed in both chloride and sulphate solutions, at 25°, with two samples of magnesium giving widely different rates of attack in sodium chloride solutions.

TABLE I.—Analyses of Metal Used.

| | | | MgUB. | MgUH. |
|---|---|---|---|---|
| Si | . | . | trace | trace |
| Al | . | . | 0·003-0·01 | 0·003-0·01 |
| Fe | . | . | trace | trace |
| Cu | . | . | 0·003-0·01 | 0·003-0·01 |
| C | . | . | trace | trace |
| Mn | . | . | 0·003-0·01 | 0·003-0·01 |
| Pb | . | . | trace | trace |
| Ca | . | . | trace | 0·003-0·01 |
| Ni | . | . | 0·003-0·01 | 0·003-0·01 |
| Na | . | . | trace | trace |
| $Mg_3N_2$ | . | . | <0·02 | <0·02 |

Spectroscopic analyses of the thin, fully annealed, sheet metal, MgUB

[4] (*a*) Evans and Hoar, *J. Inst. Metals*, 1934, **30**, 431 ; (*b*) Whitby, *ibid.*, 1933, **29**, 523, 853.
[5] *J. Iron and Steel Inst.*, 1932, **126**, 376.
[6] *J.C.S.*, 1919, **115**, 272.         [7] *Kinzoko no Kenkyu*, 1930, 283, 329.

and MgUH, are given in Table I. and were taken by the Metallurgical Dept., N.P.L., on a Hilger quartz spectrograph, type E1 ; magnesium nitride was determined by the method described previously.[1c]

Experimental technique, size of specimens and method of preparation were standard ;  all experiments were performed in duplicate. Hydrogen evolution was measured against time in sodium chloride solutions of normalities 0·001, 0·01, 0·10, 1·0, 2·0, 3·0 and 4·0 and in sodium sulphate solutions of the same concentrations up to 3·0$N$ ;  in addition, experiments were made in conductivity water.    Results, shown in Figs. 5 and 6, were calculated as cubic centimetres of hydrogen evolved per 2 minutes, or per hour, after 4 minutes and 2 or 7 hours respectively from the start of the reactions.    The curves show rate of attack against logarithm of the salt concentration in normalities, at the various stated times from the commencement of the reaction.

The results demonstrate that although maxima in the rates of attack are caused by certain salt concentrations, their actual position varies not only according to the sample of metal but also according to the time from the start of the reaction. In sodium



FIG. 5.—Effect of sodium chloride concentration on rate of dissolution of magnesium.    1 = after 4 mins., 2 = after 2 hours, 7 = after 7 hours.

chloride for example (Fig. 5) the *initial* rates of attack of MgUB did not vary in solutions of concentration up to $N$, but a slight increase occurred in 2$N$ followed by a decrease in 3$N$ and 4$N$ to almost the same rate as that given by the dilute solutions.    After 2 hours, however, the rate increased with concentration up to $N$ and then decreased in 2$N$ and 3$N$ solutions, finally increasing again, to a maximum, in 4$N$. After 7 hours, the maximum rate was given by 2$N$ solutions but the increase between 3$N$ and 4$N$ was still evident although less accentuated.

The other sample, MgUH, showed, after both 2 and 7 hours' attack, a maximum rate in 2$N$ solution with a decrease in 3$N$ and finally a well-defined increase in 4$N$ solution ;  initially, the rate in 4$N$ solution was

the greatest. The curves illustrating the later stages of the attack are n partial agreement both with those of Hughes and with those of Endo and Miyasaki, inasmuch as the maximum rate was obtained in solutions of approximately $2N$. Magnesium hydroxide solubilities, measured by the method previously described,[1a] are in agreement with the figures of Endo and Miyasaki and show a maximum at approximately $2N$.

The rise in the rate of attack in solutions of between $3N$ and $4N$ has not been described previously ; a similar rise occurs between these two concentrations in the solubility of magnesium hydroxide. The shape of the magnesium hydroxide solubility curve, although significant, is not necessarily an explanation of the shape of the last parts of the rate/concentration curves since similar curves from sodium sulphate solutions show no relation with magnesium hydroxide solubility.

In sodium sulphate solutions (Fig. 6), the two samples of magnesium gave widely different results. MgUH produced a well-defined maximum in the rate of dissolution in $2N$ solution, the rate then decreasing with further increase in salt concentration, but, unlike the results from sodium chloride solutions, not increasing again. The rate of attack of the other sample, MgUB, increased with the salt concentration up to approximately $0·1N$ and then decreased with further increasing concentration up to $N$ after which a second increase occurred.
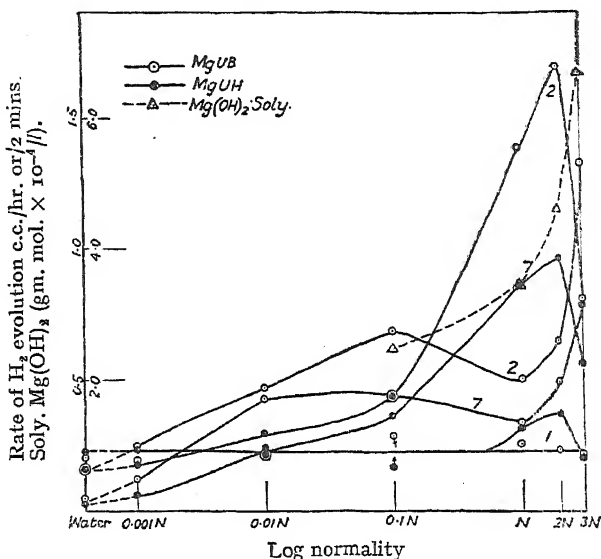


FIG. 6.—Effect of sodium sulphate concentration on rate of dissolution of magnesium. $1$ = after 4 mins., $2$ = after 2 hours, $7$ = after 7 hours.

The rates of dissolution of MgUH were initially identical in solutions of concentrations up to between $0·1N$ and $N$, after which the curve followed the shape of those resulting from increased times of immersion. MgUB produced initial rates of attack which were approximately identical throughout the concentration range. The magnesium hydroxide solubility curve shows no relation with the points of maximum attack. A remarkable fact about all these results is the large difference in the behaviour of the two samples of magnesium of almost identical composition. Both were rolled in the form of strips from the same casting, both were fully annealed and both gave reproducible results.

The identity of the initial rates of reaction is explained by assuming the same initial anode reaction of exclusive hydroxyl ion discharge, irrespective of the concentration of other anions in the solution. In concentrated solutions, however, it is possible that other anions may possess sufficient individual ion activities, compared with that of the hydroxyl ion, to ensure that the free energy of the corresponding magnesium salt

is greater than that of magnesium hydroxide. A higher initial rate of reaction must be expected in such cases and may be further increased by the presence of metallic impurities in the magnesium, capable of altering the anode potential in the requisite direction.

After many of the primary anodes have been covered with hydroxide and made cathodic to the remainder, local impoverishment of hydroxyl ions, with increase in anodic current density, normally causes other anions, if present, to discharge with the formation of either soluble salts or sparingly soluble basic compounds. The number of primary anodes that become film-covered, before other anions discharge, depends mainly upon the activities of such anions. Initially, while hydroxyl ions only are discharging, the rate of attack is probably inversely proportional to the time, since, if other variables remain constant, the protective film forms at a rate dependent only on the number and size of the primary anodes, *i.e.*,

$$dH/dt = k/t,$$

or integrated :

$$H = k \ln t, \quad . \quad (1)$$

where $H$ is the total hydrogen evolved at time $t$. In pure water (1) must hold throughout the reaction, but in salt solutions it will only hold initially, departure occurring after a time dependent, other things being equal, on the nature and activities of the extra-hydroxyl anions. The experiments on the effect of sulphate and chloride concentration enable (1) to be tested experimentally. Figs. 7 and 8 illustrate some results taken from dissolution/time curves obtained with MgUH in chloride and sulphate solutions, respectively. The persistence of the initial linearity of hydrogen evolution
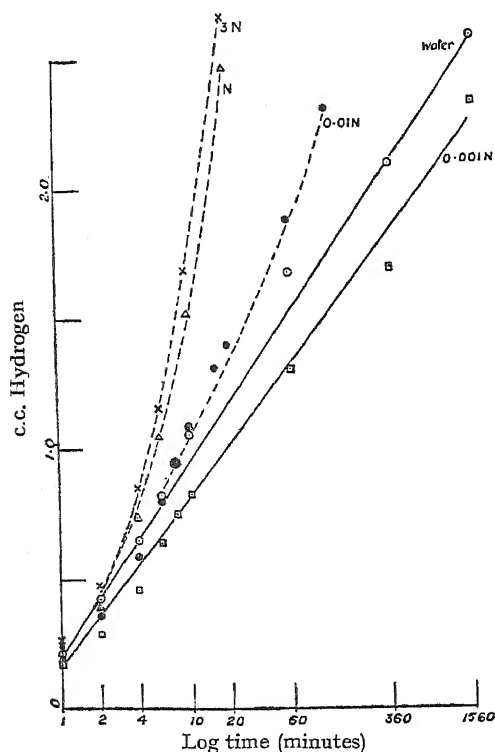


Fig. 7.—Chloride solutions.

with the logarithm of the time decreases as the concentration of the solution increases and provides, therefore, an additional confirmation of the validity of the theory of primary preferential hydroxyl ion discharge. A comparison of Figs. 7 and 8, which are both plotted to the same scale, shows that in solutions of medium concentration the initial logarithmic relationship holds for longer times in sulphate than in chloride solutions of similar normalities. Since the length of the straight line is assumed to be a measure of the persistence of exclusive hydroxyl ion discharge, the curves provide confirmation of the previously suggested [1 *d*] explanation, based on theoretical considerations, of the difference in rates of attack in chloride and sulphate solutions, respectively. Fig. 7 shows that although both water and 0·001$N$ sodium chloride solution give straight lines, the rate of attack in water becomes slightly greater than that in the very

dilute chloride solution. The explanation probably lies in the slight depression of the solubility of magnesium hydroxide in presence of even small quantities of sodium chloride. The decrease in the rate of attack of MgUH in $3N$ sodium sulphate solution in comparison with $2N$ solution (Fig. 6) is also shown in Fig. 8 and is not caused by increased persistence of exclusive anodic hydroxyl ion discharge in the more concentrated solution.

## Effect of Cation on Rates of Dissolution.

Shilov and Shatunovskaja [8] stated that the dissolution of magnesium in water is accelerated by the addition of various chlorides in the order : barium chloride > calcium chloride > potassium chloride > lithium chloride, and added that the velocity of reaction is but little affected by concentration between $0 \cdot 1 \ N$ and $N$.

The rate of anodic polarisation should increase with increasing hydroxyl ion transport number, according to the theory of primary preferential hydroxyl ion discharge. The



FIG. 8.—Sulphate solntious.

initial rate of attack, therefore, should be higher and the "secondary" rate of attack lower, in solution A than in solution B, if, other factors being equal, the transport number of OH′ in A is > transport number of OH′ in B.

Dissolution/time curves have now been obtained with samples of MgUB in $2N$, $0 \cdot 1N$ and $0 \cdot 01N$ solutions of potassium, sodium and lithium chlorides at $25°$. The potassium and sodium chloride solutions were made from Kahlbaum's purest material and laboratory distilled water, redistilled from alkaline permanganate. Kahlbaum's lithium chloride was recrystallised once from conductivity water by saturating with pure hydrogen chloride gas and then three times from conductivity water alone, finally drying in a quartz dish at $130°$ ; solutions were neutral.

Results are illustrated in Figs. 9, 10 and 11 and complete solubility figures for magnesium hydroxide in gram-molecules per litre at $25°$ are recorded in Table II.

Fig. 9 shows that in $2N$ solutions the rates of attack initially were of the same magnitude but later varied in the different solutions in the order : lithium chloride > potassium chloride > sodium chloride, whereas after attack had continued still further small differences only were shown in the respective velocities. In $0 \cdot 1N$ solutions (Fig. 10) the rates remained
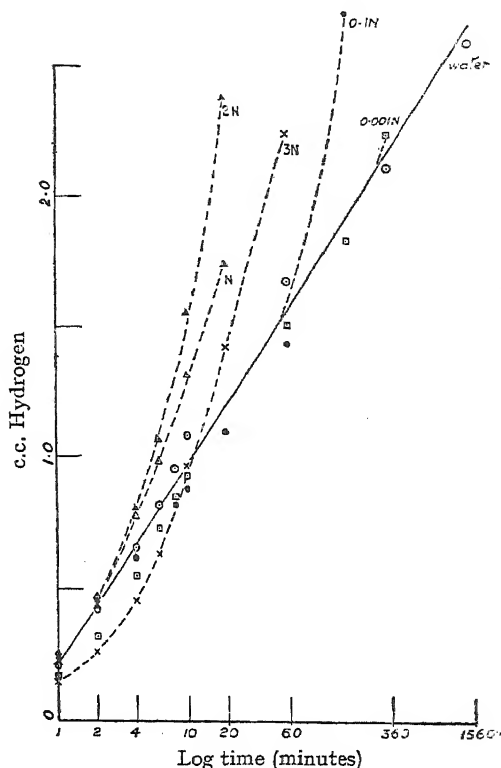
[8] *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 375.

the same throughout the course of the experiments whereas in $0 \cdot 01N$ solutions the initial order was : sodium chloride > potassium chloride > lithium chloride, but after about 12 minutes an inversion of the order
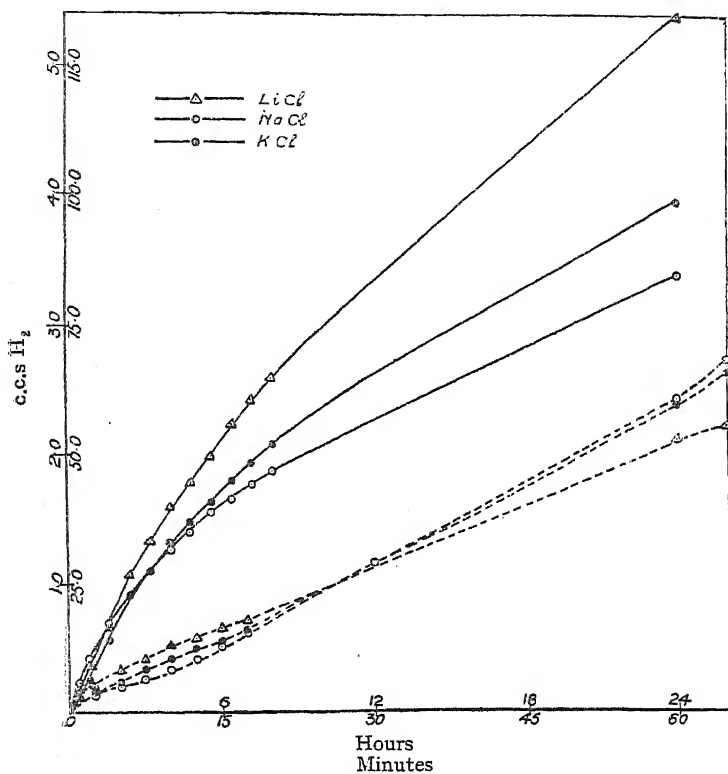


FIG. 9.—$2N$ solutions.    Broken curves are later stages.
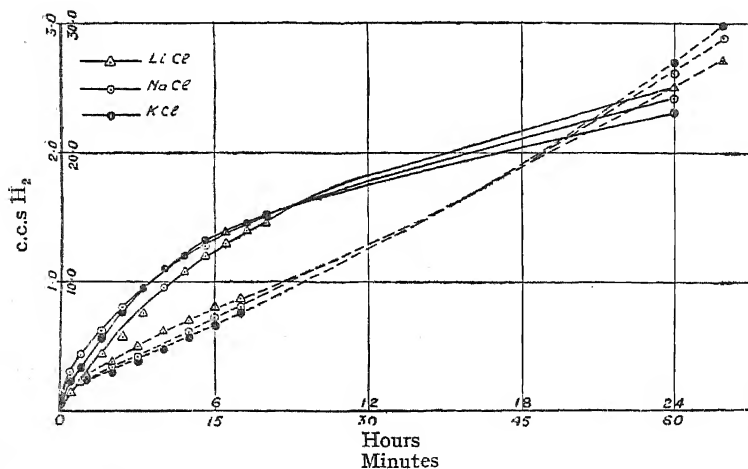


FIG. 10.—$0 \cdot 10N$ solutions.    Broken lines are later stages.

took place to show lithium chloride > potassium chloride > sodium chloride.    These    results    do    not    agree    with    those    of    Shilov    and Shatunovskaja.[8]

At all concentrations the transport number of the hydroxyl ion is
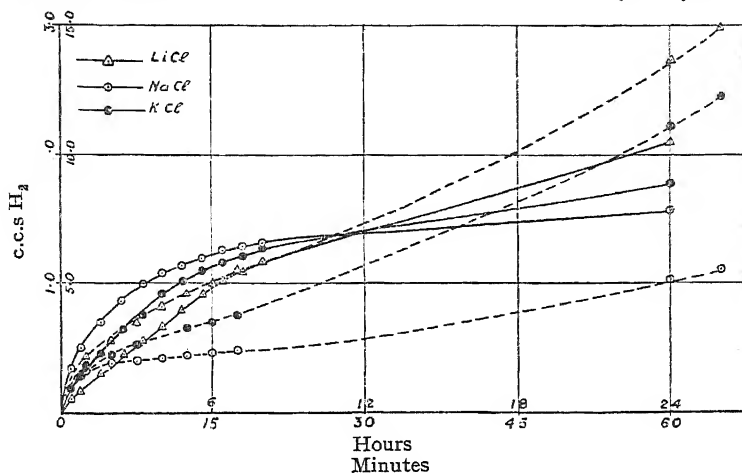


FIG. 11.—0·01$N$ solutions.    Broken curves are later stages.

greater in solutions of sodium hydroxide than in those of potassium hydroxide.[9] No figures are available for lithium hydroxide but it is known that in chloride solutions of all concentrations the anion transport number varies in the order : lithium chloride > sodium chloride > potassium chloride,[9] and it may be assumed that the hydroxyl ion transport number varies in the same manner. The curves, therefore, cannot be interpreted by a consideration only of the hydroxyl ion transport numbers. Table II. shows that in 2$N$ solutions the solubility of magnesium hydroxide varies in the order : lithium chloride > potassium chloride > sodium chloride, whereas in 0·1$N$ solutions it is almost the same in lithium and in potassium chlorides and least in sodium chloride. In 0·01$N$ solutions the highest solubility is in potassium chloride and the lowest in sodium chloride.

A further complication is possibly introduced by the increase in the ionic product of water with the ionic strength of the solution.    Harned [10] has shown that in dilute solutions of alkali metal halides the ionic product is independent of the nature of the halide present, but when the concentrations reach about 0·1$N$, the variations become marked.    In $N$ solutions $k_w \times 10^{-14}$ is for lithium chloride 1·6, for sodium chloride 1·4, and for potassium chloride 1·3.

TABLE II.—SOLUBILITIES OF MAGNESIUM HYDROXIDE AT 25°.

| Solvent. | | Solubility $\times$ 10⁻¹. |
|---|---|---|
| Na$_2$SO$_4$ | 3$N$ | 6·7 |
| ,, | 2$N$ | 4·6 |
| ,, | $N$ | 3·4 |
| ,, | 0·1$N$ | 2·5 |
| NaCl | 4$N$ | 3·0 |
| ,, | 3$N$ | 2·5 |
| ,, | 2$N$ | 3·9 |
| ,, | 0·1$N$ | 1·7 |
| ,, | 0·01$N$ | 2·7 |
| KCl | 2$N$ | 5·0 |
| ,, | 0·1$N$ | 2·5 |
| ,, | 0·01$N$ | 3·8 |
| LiCl | 2$N$ | 6·0 |
| ,, | 0·1$N$ | 2·4 |
| ,, | 0·01$N$ | 3·1 |

[9] *Internat. Crit. Tab.*, **6**, 310.
[10] *Trans. Faraday Soc.*, 1927, **23**, 462 ; *Trans. Amer. Electrochem. Soc.*, 1927, **51**, 571.

It is impossible to predict the net effect on the velocity of the anodic reactions of the variations with salt concentration of the ionic product of water, the transport number of the hydroxyl ion and the solubility of magnesium hydroxide, all of which may conceivably affect the rate of attack.   The curves show that neither the initial nor " secondary " rates of dissolution are controlled by any one of these variables.

## Summary.

No protection against subsequent dissolution in chloride and sulphate solutions is provided by increasing the thickness of the air-formed film on magnesium.   Visible films sometimes produce an increase over the normal rate of dissolution.

The effect of concentration of chloride and sulphate solutions on the rate of dissolution of magnesium therein has been investigated and the results compared with the solubility of magnesium hydroxide in the solutions.   The position of the maximum velocity depended on the sample of metal and on the time of immersion.   Analyses of the curves have provided additional evidence of primary preferential hydroxyl ion discharge.

Dissolution/time curves have been obtained from magnesium in lithium, sodium and potassium chloride solutions and the solubility of magnesium hydroxide has been measured therein.

# THE NATURE OF THE DIFFUSION OF MERCURY ON TIN.

By T. Alty and A. R. Clark.

## The Diffusion of Mercury over a Tin Surface.

When a drop of mercury is placed on a sheet of tinfoil it is found to sink into the foil and to spread over a well-defined area, forming in this way a circular or elliptical area of amalgam.   The nature of this amalgam has been investigated by Spiers [1] who has shown that, after the diffusion is complete, the mercury is uniformly distributed throughout the amalgamated area and that the area amalgamated is proportional to the mass of mercury originally placed on the tin surface.   He found further that in the amalgam the atomic percentage of mercury is about 11·8 and is constant for a six-fold variation of foil thickness. The rate of growth of the amalgam ellipse could be represented by two expressions of the type

$$A = A_\infty(1 - e^{-kt})$$

[1] F. W. Spiers, *Phil. Mag.* (7), 1933, **15**, 1048-1061.

$A_\infty$ being the final area. The first of these two expressions corresponds to the diffusion while there is still a pool of mercury present at the centre of the ellipse ; the second to the diffusion after this mercury supply has disappeared. Spiers has made an X-ray examination of the amalgamated foil and found that it consists of a hexagonal lattice with the dimensions

$$a = 3 \cdot 23\text{Å} \qquad c = 3 \cdot 00\text{Å}$$

a result in agreement with the previous work of Simson.[2] The latter found that, in the tetragonal crystal lattice of pure tin, mercury is soluble only to the extent of 1 per cent. If more mercury is added to the tin a second solid phase appears. This is a hexagonal lattice which, between 1 per cent. mercury and 8 per cent. mercury, can exist side by side with the original tin lattice. In an amalgam containing 8 per cent. mercury, the tetragonal tin lattice has completely disappeared and for higher concentrations of mercury, the hexagonal lattice is the only solid phase present. Spiers concludes that the amalgams rich in mercury consist of two phases, the hexagonal solid phase described above, which is a secondary solid solution, and a liquid phase consisting of a slight solution of tin in mercury, this liquid phase making its appearance when the concentration of mercury is 8 per cent. (atomic).

The tinfoil used by Spiers varied in thickness from about $7\mu$ to about $46\mu$ and with this very thin material the whole thickness of the foil becomes amalgamated. However, if a drop of mercury is placed on the surface of a thick block of tin, it is found that the mercury diffuses over the surface of the block very much more rapidly than it does into its volume. This therefore suggests that the diffusion process is really a combination of a comparatively rapid surface diffusion with a much slower volume diffusion. If this is the case, we may consider that the mercury diffuses essentially as a surface layer and that from this layer the slow volume diffusion takes place. The action of the latter causes a slight increase of thickness of the film of amalgam which renders it visible and so makes it possible to observe the progress of the surface diffusion directly.

A visible layer of this nature gives a very direct method of investigating the mobility of the surface film, and this paper describes an attempt to obtain information about this from an examination of the diffusion of mercury on thick pieces of tin. It has been shown that the diffusion is essentially a surface phenomenon as suggested above. The movement over the surface obeys an ordinary diffusion equation and the variation of the velocity of diffusion with temperature is of the usual exponential type, $v = v_0 e^{-E_0/RT}$. It is shown further that this velocity is dependent on the previous treatment of the tin surface, as would be expected ; that it is dependent on the nature of the medium surrounding the tin ; and that the diffusion over a surface of pure tin is quite different from that over a surface of amalgam containing 8 per cent. mercury. Such an amalgam will have the hexagonal lattice found by Spiers and Simson, while the tin lattice will, of course, be tetragonal.

## Theory.

After a number of preliminary experiments it was found most satisfactory to work with tin cylinders about 4 mm. in diameter. The

[2] Cl. v. Simson, *Z. physik. Chem.*, 1924, **109**, 183.

cylinder was suspended with its lower end immersed in pure mercury and as the latter diffused up the surface the brightly polished tin surface changed to the whitish surface characteristic of the amalgam. The junction between the two was extremely regular and sharp and with suitable illumination the motion of the boundary could be examined without difficulty.

Even when the surface film had moved a distance of several centimetres, the depth of penetration into the cylinder was found to be very small (a very small fraction of a mm.) so that the velocity of the volume diffusion is of quite a different order of magnitude from that of the surface diffusion. Consequently the amalgam never penetrated to a depth comparable with the radius of the cylinder and, in calculating the velocity of the surface diffusion, we may ignore the curvature of the cylinder and consider the diffusion as taking place at a plane surface $x = 0$, the surface being immersed in mercury up to the plane $y = 0$.

Assuming that the motion obeys the usual type of diffusion equation and that the disturbing effect of the extremely slow volume diffusion may be disregarded, we shall have

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial y^2} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

where $n$ is the number of mercury atoms per square centimetre on the surface at time $t$ and height $y$

and     $D$ is the surface diffusion coefficient.

Equation (1) has to be satisfied subject to the conditions

$$n = 0 \text{ at } t = 0,$$

and     $$n = n_0 \text{ at } y = 0,$$

since the concentration in the film at the point where it enters the liquid mercury remains constant $(n_0)$ throughout the experiment.

The solution of (1) which satisfies these conditions is

$$n = n_0 \operatorname{erf} \left( \frac{y}{2\sqrt{Dt}} \right), \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

where

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-\xi^2} d\xi.$$

Equation (2) thus gives the surface concentration of mercury atoms at a height $y$ above the liquid mercury level. Now at the sharply defined upper edge of the amalgam film, the concentration will be constant $(= n_1$ say) so that so far as the motion of this boundary is concerned, we shall have,

$$n_1 = n_0 \operatorname{erf} \left( \frac{y}{2\sqrt{Dt}} \right)$$

where $y$ is now the position of the boundary at time $t$.

Hence     $$\operatorname{erf} \left( \frac{y}{2\sqrt{Dt}} \right) = \frac{n_1}{n_0} = \text{constant},$$

and therefore     $$\frac{y}{2\sqrt{Dt}} = \text{const.} = C \text{ (say)},$$

so that
$$D = \frac{y^2}{4C^2t}$$

or
$$D \propto y^2/t$$

and the coefficient of surface diffusion will be given by the slope of the graph of $y^2$ plotted against $t$, which must be a straight line if the diffusion equation is to be satisfied. In Fig. 1, $y^2$ is plotted against $t$ and the relation between these quantities is seen to be quite linear. In the following the slope of the $y^2 - t$ graph will be denoted by $v$.

Now it is well known that under suitable conditions the temperature variation of the diffusion constant $D$ of a surface film has the form

$$D \propto e^{-E_0/RT}$$

where $E_0$ cals./ gram atom is the minimum energy which must be possessed by the



FIG. 1.

atoms of the surface film before they become mobile and therefore able to diffuse along the surface and $R$ is the gas constant per mole. If we may treat the diffusion of the mercury over the tin surface as a similar process we should have

$$v = y^2/t \propto D \propto e^{-E_0/RT},$$
so that
$$\log_e v = A - E_0/RT \quad . \qquad . \qquad . \qquad . \qquad (5)$$
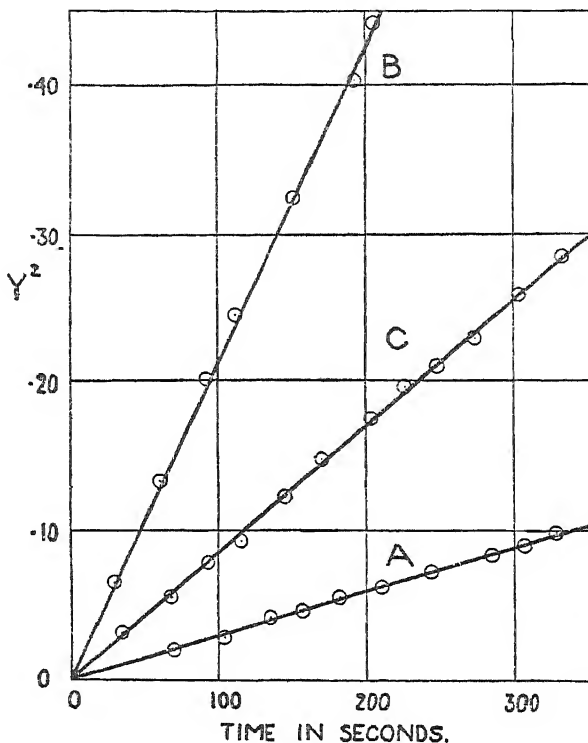
## Experimental.

Clean mercury was filtered into a wide glass tube which was immersed in a thermostat and held rigidly in position to avoid any movement of the mercury during an experiment. The tin cylinder to be used was clamped to the end of a long screw which passed through a heavy brass collar which in turn was screwed to the side of the thermostat. By this means the tin could be raised or lowered without causing any disturbance in the mercury. It was necessary to make an electrical connection between the mercury and the thermostat as otherwise the mercury became charged during the filtering, etc., and discharged itself on to the tin cylinder when

the latter was lowered towards the mercury. This often caused the mer-· cury to make rather uneven contact with the tin so that the amalgam level was not uniform round the cylinder. All difficulty of this nature was removed when the mercury was connected with the surrounding water.

In an experiment the cylinder was left 1 cm. to 2 cm. above the surface of the mercury for some time until both had reached the temperature of the thermostat. The cylinder was then lowered until its lower end entered the mercury which immediately wetted it and rose in the form of a meniscus. From this meniscus the amalgam film at once appeared and its motion along the cylinder was measured by means of a low power travelling microscope. The position of the amalgam boundary was observed each half-minute and its distance from the top of the meniscus obtained. The square of this distance was plotted against the time ; the meniscus level was once more measured at the end of the experiment.

To form the cylinders pure tin was melted in an evacuated pyrex vessel to which were attached a number of 5 mm. pyrex tubes. The molten metal was allowed to flow into these tubes which were then sealed off and left to cool slowly in an oven. The cylinders so formed were turned and carefully polished before use.

The amalgam cylinders used in the later experiments were constructed in the same way, the correct proportions of tin and mercury being sealed together in the evacuated vessel. They were kept in the liquid state for a considerable time to ensure thorough mixing of the two constituents and were then cast as before.

### Variation of the Velocity of Diffusion with the State of the Surface.

As soon as the experiments were begun it was found that the graphs of $y^2$ against $t$ were linear but that successive experiments were very in- consistent and gave very varied values of $v$ for experiments which should have been identical. The only possible variable was the state of the tin surface so, as a test of the effect of the surface condition, three cylinders from the same sample of tin were given different surface treatment. The cylinder A was turned in a precision lathe and used just as it came from the lathe ; B was turned and then polished with the finest grade of emery paper while C was turned and given a mirror-like polish by means of cotton wool soaked in water. This treatment was found to be the most effective method of producing a high polish on the tin.

The results obtained with these cylinders are shown in Fig. 1. It is seen that the diffusion is slowest on the unpolished specimen and fastest on that polished with emery. In the case of the unpolished specimen circular grooves would be left by the lathe tool, and the actual distance to be travelled per unit length of cylinder by a surface film moving over these ridges would be greater than in the case of a smooth surface. When polished with emery these circular ridges are removed by moving the emery longitudinally along the tin cylinder while the latter rotates in the lathe, a process which covers the surface with an irregular mass of tiny scratches. The final polishing with cotton removes these also and leaves a highly polished surface over which the mercury diffuses at a somewhat lower rate than over the surface treated with emery.

These experiments support the idea of a surface diffusion, as a volume phenomenon would not be expected to be so sensitive to the state of the surface.

Since the circular grooves left by the lathe tool on cylinder A are approximately at right angles to the direction of the diffusion, the dif- fusing mercury will move over a regular array of hills and valleys on the tin surface. We can obtain some idea of the degree of roughness of this turned surface by comparing the rate of diffusion on it with that on the polished tin cylinder (C). From Fig. 1 we find that at any time $t$

$$y_A^2 = 0 \cdot 351 \, y_c^2.$$

But since the temperature is the same in both experiments the mercury must diffuse an equal distance *along the actual surface* of the two cylinders, so that if $z_A$ is the true distance travelled along the surface of A,

$$y_c{}^2 = z_A{}^2$$

and so $\qquad z_A{}^2 = y_A{}^2/0.351, \quad \text{or} \quad z_A/y_A = 1.69,$

or the true surface area of the turned cylinder $= 1.69$ (its apparent area).

The above results indicate that some standard surface must be used if different experiments are to be comparable. At first an attempt was made to standardise the highly polished surface by keeping one polished sample as a standard and polishing all the cylinders to the same brightness as the standard. The results were fairly consistent but were hardly as good as was desirable and a second method of preparing the surface was adopted. This was to turn the cylinder down until its diameter was very little greater than the standard used in the experiments and then use a precision lathe with an automatic feed to take off the last layers. The process was finished by removing a thickness of $1/1000$ inch in this purely mechanical manner and the surface so produced was very uniform and bright and was reproducible. The lathe tool and the cylinder were thoroughly cleaned before the preparation of each cylinder and the latter was transferred from the lathe to the apparatus by means of a pair of forceps so that the tin surface was kept as free from contamination as possible.

With the surface prepared as above, successive experiments gave very reproducible results but after a few experiments there appeared to be a slow and steady change in the velocity of diffusion. This was found to be due to the effect of the tin on the cutting edge of the lathe tool which, after a few experiments, required resharpening. This process may have a very noticeable effect on the velocity. Consequently the final method of obtaining the values of $v$ at different temperatures was to use two similar thermostats, one at a temperature $T_1$ and the other at $T_2$, and perform experiments in them alternately. Usually from four to six experiments were performed in each thermostat and the average values of $v$ at each of the two temperatures, and therefrom $v_2/v_1$, were obtained. The tool was resharpened and then $T_2$ was compared with a new temperature $T_3$ and the ratio $v'_3/v'_2$ obtained in the same way. In general the values $v_2$ and $v'_2$ will be different for the two different settings of the lathe tool. However, if we take the surface $T_1$ as a standard, then the velocity at $T_2$ will be $v_2$ while the second set of experiments indicates that the velocity at $T_3$ is $\left(\dfrac{v'_3}{v'_2}\right)$ of that at $T_2$, *i.e.*, the velocity at $T_3$ is $\left(\dfrac{v'_3}{v'_2}\right)v_2$.

In this manner any variation in the velocity due to variations in the surface conditions can be eliminated and the variation of velocity with temperature can be obtained for a standard surface. As a test of the method experiments were made at $30°$ and $60°$, $60°$ and $90°$, and then at $90°$ and $30°$ and the two values of the velocity at $30°$, the one obtained directly and the other deduced in the above manner, agreed closely.

### The Temperature Variation of D.

The diffusion was examined at a number of temperatures between $2°$ C. and $93°$ C. At $93°$ C. it was not possible to leave the tin cylinder suspended above the mercury to acquire the temperature of the bath because of the mercury vapour present. It was only at this temperature that any difficulty of this sort was experienced but after being suspended above the hot mercury for some minutes, the tin surface became spotty and the diffusion was very irregular. For this reason the tin and its supporting screw were placed in an empty glass tube in the thermostat until they had reached temperature equilibrium. They were then transferred to the experimental vessel and the experiment was commenced at once.

A typical set of measurements of $v$ at 60° C. is shown in Table IA. and the averages of the ratios $(v_{T_1}/v_{T_2})$ are given in Table IB.

TABLE IA.

TABLE IB.

| Expt. No. | Temp. | $v_{60}$. | $T_1$. | $T_2$. | $v_{T_1}/v_{T_2}$. |
|---|---|---|---|---|---|
| 1 | 60·1 | 0·0246 | 30 | 60 | 0·747 |
| 2 | 60·0 | 0·0250 | 90 | 60 | 1·295 |
| 3 | 59·9 | 0·0252 | 44 | 60 | 0·872 |
| 4 | 60·0 | 0·0252 | 15 | 45 | 0·731 |
| | | | 75 | 50 | 1·230 |
| Average value of $v_{60} = 0·0250$. | | | 30 | 2 | 0·93 |

From the ratios $v_{T_1}/v_{T_2}$ and the standard value $v_{60}$, the rate of diffusion at different temperatures can be calculated and $\log_e v$ may then be plotted against $1/T$. This is done in Fig. 2. The value of $E_0$ determined from this graph is found to be

$$E_0 = 1920 \text{ cal./gram atom.}$$

It will be observed that the point at 2° C. lies much above the graph of Fig. 2. Considerable difficulty was experienced in obtaining this point as at this temperature the tin amalgamates with the mercury very slowly and it was rather troublesome to get the amalgam film started uniformly. When this had been done a linear relation could not be obtained between $y^2$ and $t$ as the rate of increase of $y^2$ with $t$ increased for some time after the beginning of an experiment. This is shown in Fig. 3. It was considered possible that
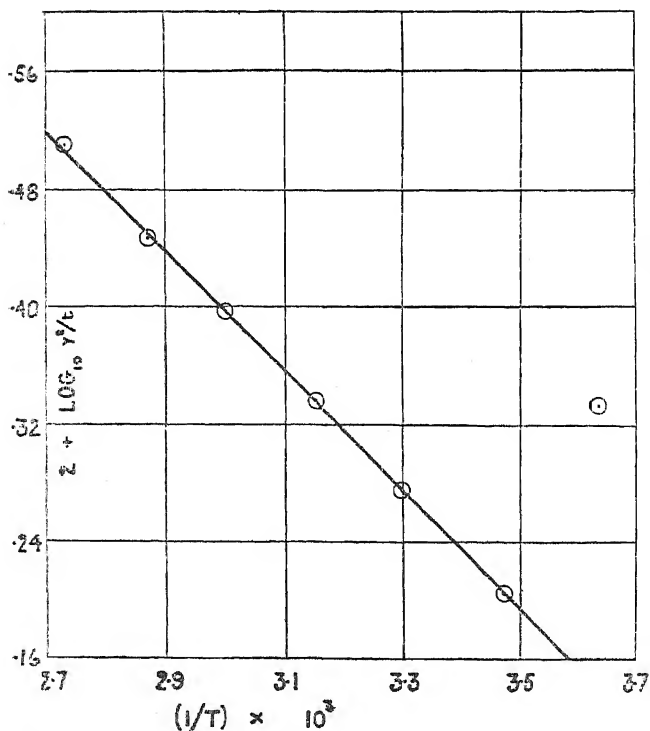


FIG. 2.

this was due to a temperature gradient up the tin cylinder. This might be present if the heavy brass bearing and the screw holding the tin were

not thoroughly cooled before the experiment commenced. However a vessel filled with ice was attached to the brass block holding the screw and tin cylinder so that any such temperature gradient would be eliminated, but the curve of Fig. 3 was still obtained. After a little time from the start of the experiment the points lay near to a straight line and this line was used to determine the point shown in Fig. 2. Its position is much less reliable than that of the other points but there is little doubt that it lies well above the line of Fig. 2. The velocity at 2° C. was compared both with that at 15° C. and that at 30° C. and both sets of experiments indicated that the point at 2° C. was above that at 15° C.



Fig. 3.

### The Influence of the External Medium.

If the diffusion is due to the motion of a surface layer, this motion will depend on the nature of the potential field at the surface and this may be modified by changing the medium surrounding the tin cylinder, from air to (say) a liquid. The film will then move along the tin-liquid interface and any effect of the liquid on the mobile surface atoms will show itself as a change in the rate of diffusion.

To obtain information on this point two sets of experiments were performed the first in oil and the second in water. These liquids were chosen for their dissimilar properties so that the change with the molecular nature of the liquid could be examined.

For the oil experiments a pure light liquid petroleum was used, the mercury reservoir in the experimental vessel being covered to a depth of several centimetres with the oil. The tin cylinder, after being prepared in the lathe was heated *in vacuo* in a vessel containing some of the oil so as to drive off as much of the adsorbed air film as possible from the tin surface and so allow the oil to make a close contact with it. The tin was left to cool in the evacuated vessel and was then immersed at once in the oil in the experimental vessel. During this procedure a thick oil film adheres to the tin so that the surface is not exposed to the air directly. The method of experimenting was the same as in the air experiments but measurements could not be made at low temperatures owing to the difficulty of making the tin and mercury amalgamate. Hence the experiments were confined to a single temperature of 60° C., at which the
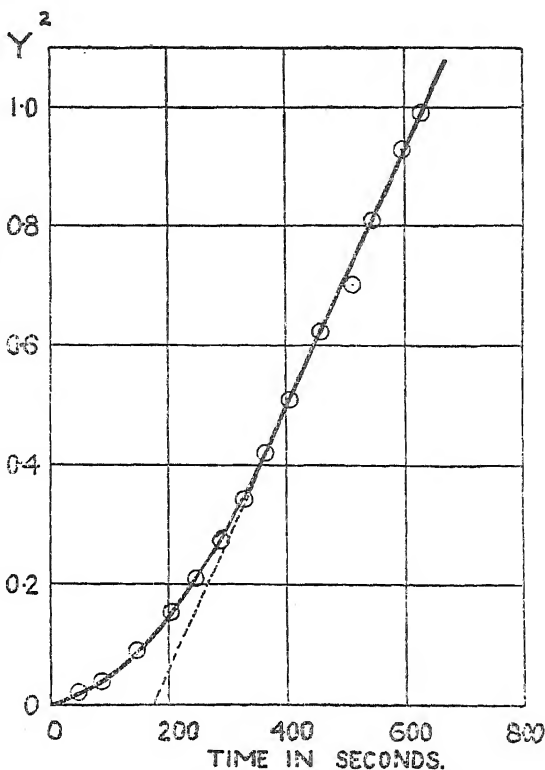
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amalgamation was satisfactory and the rate of diffusion in oil was compared with that at the same temperature in air by performing experiments in air and oil alternately. The results appear in Table II. which shows that the rate of diffusion in oil is about 0·77 of that in air at 60° C.

TABLE II.

| Expt. No. | $y^2/t$. | Temp. °C. | Surface. |
|-----------|----------|-----------|----------|
| 1 | 0·0130 | 60·4 | paraffin |
| 2 | 0·0168 | 60·6 | air |
| 3 | 0·0130 | 60·6 | paraffin |
| 4 | 0·0170 | 60·6 | air |

Average ratio of slopes=130/169=0·77.

It is possible that this reduced rate is due to the presence of an oil film separating the liquid mercury from the tin and so reducing the supply of mercury atoms. This might be the case at the lower temperatures but at 60° C. the amalgamation was good. The cylinder was lowered well into the mercury and the latter wetted it and rose in a meniscus round it just as in air. Therefore it does not seem probable that this is the cause of the reduction.

Now from equation (5) we have

$$\log_e v = A - E_0/RT$$

and if $E_a$, $E_p$ are the energies of activation for the film in air and paraffin respectively and $v_a$ and $v_p$ are the corresponding values of $y^2/t$, then

$$\log_e \frac{v_a}{v_p} = \frac{1}{RT}(E_p - E_a),$$

or

$$E_p = E_a + RT \log_e v_a/v_p.$$

In this way an estimate of $E_p$ may be obtained and the value so found is

$$E_p = 1920 + 173 = 2093 \text{ cal./gram atom.}$$

TABLE III.

| Date. | Expt. No. | $v$. | Temp. | $(v_w/v_a)$. | Surrounding Medium. |
|-------|-----------|------|-------|--------------|---------------------|
| 27/4/33 | 1 | 0·0152 | 60·0 | | water |
| 27/4/33 | 2 | 0·0140 | 60·0 | 1·085 | air |
| 1/5/33 | 3 | 0·0190 | 60·0 | | water |
| 1/5/33 | 4 | 0·0174 | 60·2 | 1·090 | air |
| 1/53/3 | 5 | 0·0186 | 60·3 | 1·070 | water |
| 1/5/33 | 6 | 0·0172 | 60·3 | 1·080 | air |
| Average $(v_w/v_a)$ at 60° C. = 1·081. | | | | | |
| 4/5/33 | 7 | 0·0088 | 17·0 | | water |
| 4/5/33 | 8 | 0·0082 | 17·0 | 1·073 | air |
| 8/5/33 | 9 | 0·0091 | 15·0 | | air |
| 8/5/33 | 10 | 0·0098 | 15·0 | 1·076 | water |
| 8/5/33 | 11 | 0·0088 | 15·0 | | air |
| 8/5/33 | 12 | 0·0095 | 15·0 | 1·079 | water |
| Average $(v_w/v_a)$ at 15·3° C. = 1·076. | | | | | |

The experiments with water were similar to the above but when the tin cylinder was boiled in distilled water to free it from air, the surface became somewhat discoloured and lost its original brightness. For this reason the procedure was varied slightly and, instead of boiling the cylinder in water, it was placed in cold air-free water for some time. This had no noticeable effect on the surface and should be effective in removing the air from the surface irregularities.

Two sets of experiments were performed, one at 60° C. and the other at 15° C., the diffusion under water being compared with the diffusion in air in each case. The results are given in Table III. It is rather surprising to find that the rate of diffusion under water is about 8 per cent. faster than that in air. This result could certainly not be due to any such resistance effect of a water film as was discussed in the case of the oil experiments and must be ascribed to the influence of the water molecules on the surface layer.

### The Diffusion over an Amalgam Surface.

As the crystal structure of tin is changed from the tetragonal form to the hexagonal form by the addition of 8 per cent. (atomic) of mercury it was considered advisable to examine the effect of this change on the diffusion. For this purpose cylinders of 8 per cent. amalgam were used in air. The boundary of the diffusing mercury is quite uniform but the difference in the appearance of the surface on its two sides is not so great as with pure tin. There is, however, quite sufficient contrast to enable measurements to be made.
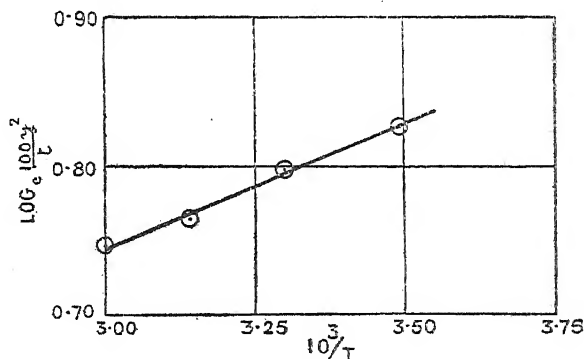


FIG. 4.

The ratio of the rate of diffusion over the amalgam to that over pure tin was determined in the usual way at temperatures of 60° C., 45° C. and 30° C. From these ratios and the known rates of diffusion over pure tin as given in Fig. 2, the rates over an amalgam cylinder having the same standard surface as that used in the experiments of Fig. 2 were obtained and the logarithms of these rates have been plotted against $1/T$ in Fig. 4. To confirm these results the rate of diffusion over an amalgam cylinder at 60° C. was compared directly with that over an amalgam cylinder at 13° C. The ratio of these rates gave a point for 13° C. (shown in Fig. 4) which lay on the straight line determined by the direct comparison of amalgam and tin.

In the above Table $v_a$ refers to the amalgam and $v_t$ to the tin. $v_{13}$ and $v_{60}$ are the values of $(y^2/t)$ on amalgam at 13° C. and 60° C. respectively.

It will be seen from Fig. 4 that the diffusion over the amalgam cylinder is very different from that over pure tin in that the temperature coefficient is reversed on the amalgam and the rate of diffusion increases with reduction of the temperature. This result was rather unexpected and is difficult to account for theoretically. However a considerable number of experiments were performed and all were consistent in showing this negative temperature effect. According to Spiers, the mercury in

TABLE IV.

| Expt. No. | Temp. | $v.$ | $v_a/v_t.$ | $v_t$ from Fig. 2. | Surface. |
|---|---|---|---|---|---|
| I | 30·1 | 0·0210 | | — | amalgam |
| | | | 1·135 | | |
| 2 | 30·0 | 0·0185 | | — | tin |
| | | | 1·178 | | |
| 3 | 30·0 | 0·0218 | | — | amalgam |
| | | | 1·204 | | |
| 4 | 30·0 | 0·0181 | | — | tin |
| | | | 1·193 | | |
| 5 | 30·0 | 0·0216 | | — | amalgam |
| | | | 1·155 | | |
| 6 | 30·0 | 0·0187 | | 0·0189 | tin |

Average $(v_a/v_t) = 1·173$
so that $v_a = 1·173 \times 0·0189 = 0·0222$ at 30° C.

| | | | | | |
|---|---|---|---|---|---|
| 7 | 60·0 | 0·0160 | | — | amalgam |
| | | | 0·843 | | |
| 8 | 60·0 | 0·0190 | | — | tin |
| | | | 0·843 | | |
| 9 | 60·0 | 0·0160 | | — | amalgam |
| | | | — | | |
| 10 | 60·0 | 0·0178 | | — | amalgam |
| | | | 0·849 | | |
| 11 | 60·0 | 0·0210 | | 0·0250 | tin |

Average $(v_a/v_t) = 0·845$
so that $v_a = 0·845 \times 0·0250 = 0·0211.$

| | | | | | |
|---|---|---|---|---|---|
| 12 | 45·2 | 0·0138 | | — | amalgam |
| | | | 0·986 | | |
| 13 | 45·2 | 0·0140 | | — | tin |
| | | | 1·014 | | |
| 14 | 45·2 | 0·0142 | | — | amalgam |
| | | | 0·974 | | |
| 15 | 45·2 | 0·0146 | | 0·0217 | tin |

Average $v_a/v_t = 0·991.$
so that $v_a = 0·991 \times 0·0217 = 0·0215.$

| | | | $v_{13}/v_{60}.$ | $v_{60}.$ | |
|---|---|---|---|---|---|
| 14 | 13·3 | 0·0262 | | — | amalgam |
| | | | 1·092 | | |
| 15 | 60·1 | 0·0240 | | — | amalgam |
| 16 | 60·0 | 0·0120 | | — | amalgam |
| | | | 1·083 | | |
| 17 | 13·0 | 0·0130 | | — | amalgam |
| 18 | 13·0 | 0·0158 | | — | amalgam |
| | | | 1·083 | 0·0211 | |
| 19 | 60·0 | 0·0146 | | | amalgam |

Average $v_{13}/v_{60} = 1·086$
so that $v_{13} = 1·086 \times 0·0211 = 0·0229.$

an amalgam in excess of 8 per cent. is present in the liquid form. Thus in the present experiments on an 8 per cent. amalgam, the mercury from the surface must enter this liquid phase instead of, as in the pure tin experiments, forming a solid solution in the tin. The exceptional be-

haviour of the diffusion on an amalgam rod must be intimately connected with this change in the condition of the mercury in the solid.

If the value of $E_0$ is calculated in the usual manner from Fig. 4 it appears that

$$E_0 = -328 \text{ cal./gram. atom.}$$

### Summary.

The diffusion of mercury in tin has been examined. It has been shown that this diffusion consists of a rapid surface diffusion accompanied by a much slower volume diffusion. The surface phenomenon has been studied in detail and appears to be a true diffusion in that it obeys an ordinary diffusion equation. The variation of the rate of diffusion with temperature also obeys the same law as that of an adsorbed film, and the energy of activation of the mobile atoms on a pure tin surface is found to be

$$E_0 = 1920 \text{ cal./gram atom.}$$

The rate of diffusion is found to be dependent on the nature of the medium surrounding the tin, being faster in water and slower in oil than in air.

The diffusion on a surface of tin amalgam containing an atomic percentage of 8 per cent. mercury is found to have a negative temperature coefficient.

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# THE KINETICS OF SORPTION PROCESSES OF HYDROGEN ON IRON.

## By N. M. Morozov.

By introducing the concept of "activated adsorption" Taylor [1] gave a formal kinetic explanation of such abnormalities as take place in the sorption of gases at high temperatures. From the point of view of kinetics there can, however, be other interpretations of these abnormalities. Ward [2] and Steacie [3] explained the slow sorption process at high temperatures from the standpoint of diffusion along grain boundaries and planes of weakness or of solution through the lattice, while Lennard-Jones [4] has pointed out that the same phenomenon may be interpreted from the standpoint of lateral migration of the gaseous particles from the more active spots of the surface to the less active ones.

It is, in general, very difficult to find out whether the slow sorption process is a solution or a surface process owing to the formal similarity of the kinetic equations used. [5] The qualitative method which Howard [6]

[1] H. Taylor, *J. Amer. Chem. Soc.*, 1931, **53**, 576.
[2] Ward, *Proc. Roy. Soc.*, 1931, A **133**, 506, 522 ; *Trans. Faraday Soc.*, 1932, **28**, 398.
[3] Steacie, *J. Physic. Chem.*, 1931, **35**, 2112.
[4] Lennard-Jones, *Trans. Faraday Soc.*, 1932, **28**, 333.
[5] H. Taylor, *Trans. Faraday Soc.*, 1932, **28**, 444.
[6] Howard, *Trans. Faraday Soc.*, 1934, **30**, 278.

employed to show that the activated adsorption takes place on the surface has been more effective. Howard has shown that van der Waals' adsorption of hydrogen on chromium oxide is diminished by the activated adsorption.

The kinetic examination of Taylor's conception is not, however, thus made less important. According to Taylor's conception several kinds of activated adsorption may take place simultaneously on the surface of the same catalyst, *i.e.*, several slow processes differing from each other both in the heat of adsorption and the activation energy, and thus occurring over different temperature ranges. Experimental evidence of this has been given by Taylor and Strother,[7] who have shown that there are two types of activated adsorption for the sorption of hydrogen by zinc oxide differing in their heats of activation : about 5 Cals. for a process occurring at temperatures ranging from 0° to 110° and about 12 Cals for a process above 100°.

At an earlier date Benton and White [8] also called attention to the existence of two slow processes for the sorption of hydrogen by iron and copper. They regarded the first (the one taking place at a lower temperature) as activated adsorption, while the second (at a higher temperature) was ascribed by them to solution from purely qualitative considerations. Such a conclusion, however, cannot be considered as well founded without a kinetic examination of the two processes, for the second slow process may be regarded as a second type of activated adsorption for equally sound reasons.

It is evident, however, that the fact of a simultaneous occurrence of both slow surface sorption and solution on the same catalyst is of much importance in solving the above-mentioned problem of the nature of sorption abnormalities in general.

The purpose of the present research was to examine the nature of sorption phenomena taking place in the sorption of hydrogen by iron at high temperatures, to separate as far as possible the several super-posed processes and to describe the nature of each individual process from the point of view of kinetics.

## Apparatus and Experimental Methods.

A quartz vessel, containing a 24·0 gr. sample of the catalyst, was placed into a thermostatic furnace and was connected by means of a tap to a gas space and a measuring system. The latter consisted of three pressure gauges : an ordinary mercury gauge for pressures exceeding 4 mm., a rotating gauge for pressures ranging from 4 mm. to $10^{-2}$ mm., and a McLeod gauge for those from $10^{-2}$ to $10^{-6}$ mm.

The amount of gas adsorbed was measured by the fall of pressure. The amount of gas evolved by the catalyst in the course of desorption could be measured by pumping off the gas into the measuring system with Töpler and Langmuir pumps.

The catalyst was made ready for fresh runs by out-gassing with Langmuir pumps at 400° for twenty-four hours (to a pressure of $10^{-5}$ mm.). The catalyst—pure iron—was prepared from iron oxide obtained by pre-cipitating iron nitrate with ammonia. The reduction of the oxide was carried out in a stream of hydrogen first for 100 hours at 200-300°, then for 280 hours at 400° and finally for 70 hours at 460°.

Although the catalyst was reduced within comparatively moderate

[7] H. Taylor and Strother, *J. Amer. Chem. Soc.*, 1934, 56, 586.

[8] Benton and White, *J. Amer. Chem. Soc.*, 1932, 54, 1821. Benton, *Trans. Faraday Soc.*, 1932, 28, 202.

temperature ranges (460° C.), the reduction was complete and the surface was practically free from oxide owing to the very long time of reduction, as stated above.    The amount of hydrogen pumped off after an adsorption corresponded to that adsorbed and no water vapour was detected.    Finally, the stability of the catalyst in the course of more than six months of work proved that the surface was free from oxide.    It is evident that, if oxide had been present, the activity of the catalyst would not have remained constant from experiment to experiment.

   The use of a higher temperature (460°) for a preliminary thermal treatment of the catalyst, as compared with the maximum temperature (400°), employed in subsequent experiments, ensured the stability of the catalyst and thus the reproducibility of sorption isotherms in the course of several months of work.

### Isobars of Sorption.

   The typical van der Waals' adsorption observed at very low temperatures (— 190°) diminishes rapidly with increasing temperature.
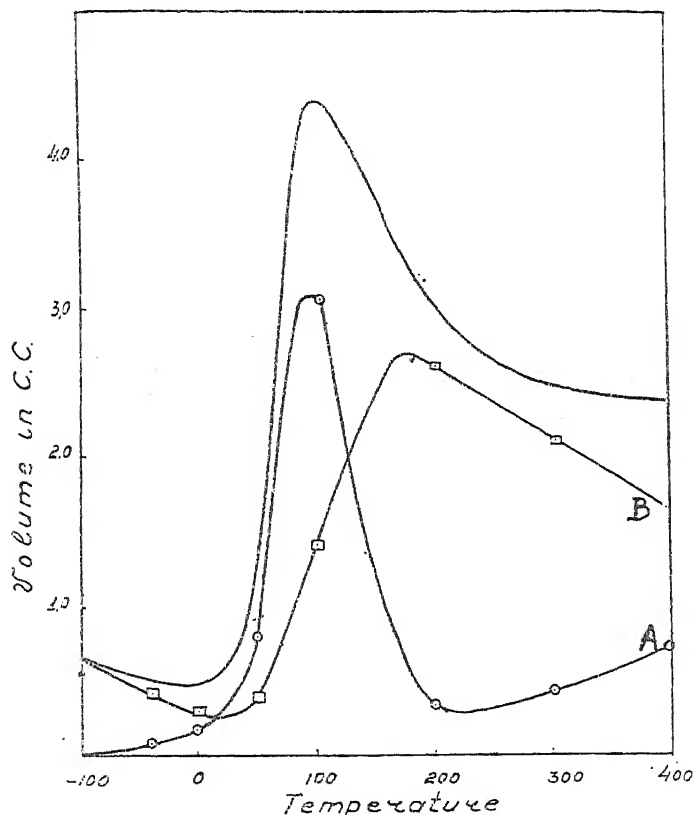


FIG. 1.—Isobars of sorption of hydrogen on iron (at 10 mm.).    A—Slow sorption. B—Instantaneous sorption.    C—Total sorption.

It is known, that a rapid attainment of equilibrium, which is in fact reached within one minute, is characteristic of this kind of adsorption.

   Even at a temperature of — 40°, however, the setting in of an additional subsequent sorption of gas may be observed after the lapse of

one minute.   This additional sorption, still very slow at − 40°, becomes more and more pronounced as higher temperature ranges are reached, increasing in rate as well as in absolute value.   This fact points to the setting in of quite a new sorption process.   The enormous difference existing between the rate of the van der Waals' adsorption and that of the new process (" activated adsorption ") enables us easily to distinguish between them within a given temperature range by separating the instantaneous sorption from the subsequent sorption, and to obtain the isotherms for both the instantaneous and slow sorption at every temperature.   The change in these isotherms following a change in
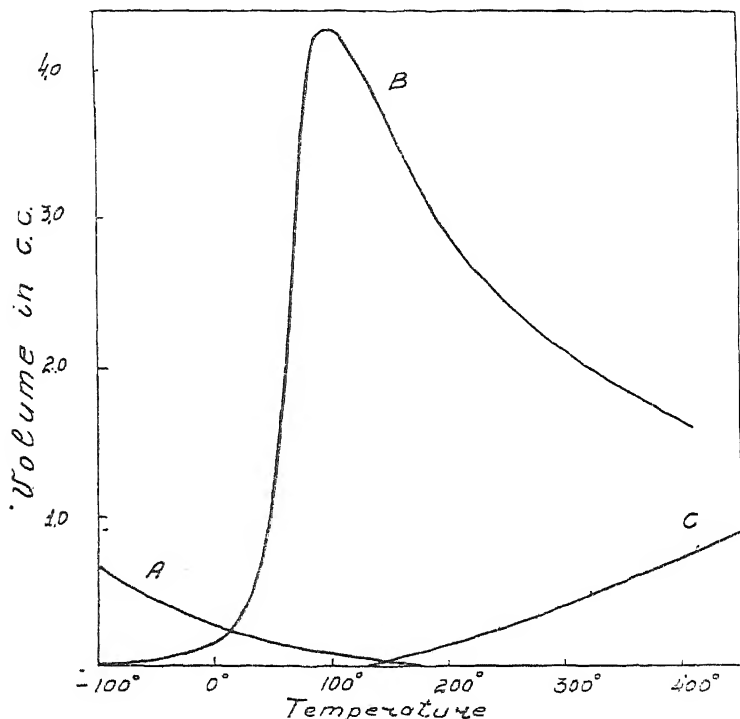


FIG. 2.—Isobars of sorption of hydrogen on iron (at 10 mm. Hg.). A—V. d Waals' adsorption.   B—Activated adsorption.   C—Activated diffusion.

temperature may be characteristic of such changes as take place in the nature of sorption in this transitional temperature region.

The rate of activated adsorption increases rapidly with increasing temperature and even at 150° to 200° it becomes almost instantaneous. It is obvious, that if when in this range of temperature a new slow sorption process sets in, it may be easily traced by obtaining the isotherms as described above.

We have used this method over the whole of the temperature range from − 190° to + 400° C., and obtained the pseudo-isotherms or the kinetics isotherms corresponding to the immediate sorption (within one minute) and the subsequent slow sorption (within one hour).   From these isotherms the corresponding pseudo-isobars of immediate and slow sorption at a pressure of 10 mm. were obtained.

The shape of the isobars, given in Fig. 1, enables us to come to a conclusion as to the temperature limits, within which the individual processes take place. The isobar of slow sorption (curve A) has two rising sections; the first (from − 100 to + 90°) must wholly belong to activated adsorption, while the second (above 250°) points to the setting in of a new slow sorption process. This process, as will be shown later, is activated diffusion or solution. The range of minimum (from 150° to 250°) is the result of a superposition of the two processes —activated adsorption and diffusion. The two processes can be roughly distinguished by means of a graphic extrapolation of the ascending and descending sections of the isobar.
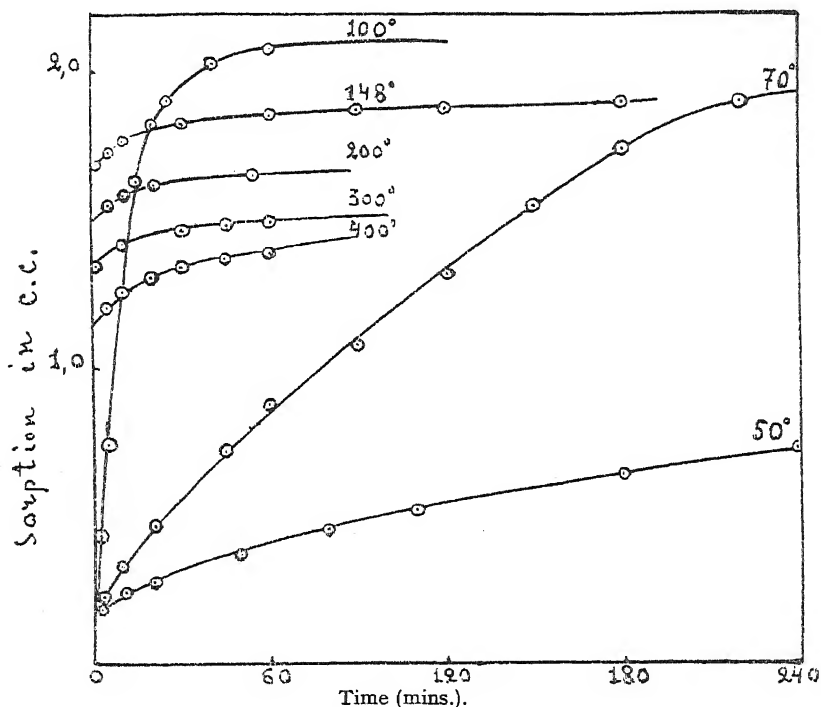


FIG. 3.—Sorption of hydrogen on iron at different temperatures.

As to the isobar, of instantaneous sorption (curve B), it may be said that its descending section (from − 190° to + 30°) corresponds almost entirely to the van der Waals' adsorption while the second descending section (above 180°) belongs entirely to activated adsorption. Within the range from + 30° to + 180° the two processes are superposed, but can be separated by means of extrapolation.

Thus by studying the pseudo-isobars of sorption we can come to the conclusion that there must exist three different kinds of sorption within the temperature range of − 190° to + 400° C., the graphs indicating which temperature ranges are most convenient for a separate investigation of each of these sorption processes.

In Fig. 2 are given the isobars corresponding to the different sorption processes.

## The Reversibility of Sorption.

An investigation of the reversibility of sorption at various tempera-
tures may also help us in tracing the temperature ranges, within which
the setting in of a new sorption process takes place.    The data obtained
in such a manner have confirmed the conclusion we have come to above.

Over the temperature range of from — 190° to — 100° the sorption
isopickns are entirely reversible.    In the interval between — 100°
and + 100° the amount of gas adsorbed irreversibly increases with
increasing temperature.    This is just the amount of gas taken up in
the course of the slow process and corresponding to the increasing
activated adsorption.    In the interval between + 100° and 150° to 160°
the sorption isopickns again become reversible.    This is the range
wherein a normal decreasing isobar of activated adsorption and of the
remains of van der Waals' adsorption is observed.    Finally, beyond
150° the reversibility of isopickns is again slowly disturbed.    This
exactly corresponds to the setting in of a new slow process, i.e., activated
diffusion.

## The Kinetics of Sorption Processes.

Fig. 3 shows the kinetics of sorption processes at temperatures from
+ 50° to 400° (with an initial pressure of 2·3 mm.).    The rate of sorption
increases    rapidly
with a rise in tem-
perature.    Even at
148°    the    largest
part    of    the    gas
(about 90 per cent.)
is taken up within
the first minute.

These    kinetic
curves are thus seen
to    agree    entirely
with    the    conclu-
sions    arrived    at
above as to the
temperature ranges,
within    which    the
different    sorption
processes    take
place.

Thus, the curves
at    50°,    70°,    100°
and    148°    represent
the kinetics of ac-
tivated adsorption.
The    curves    at
300° and 400° cor-
respond to the pro-
cess of diffusion for



Fig. 4.—The amount of slow sorption as a function of
the time (for hydrogen on iron).

the activated adsorption at these temperatures would take place
instantaneously (this will be shown below by means of the temperature
coefficient).

The different nature of these two slow sorption processes is seen from

Fig. 4. Here the amount of hydrogen taken up slowly is represented as a function of time according to the diffusion equation given by Ward,[2]

$$S = A\sqrt{D} \cdot q\sqrt{t} \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

where $S$ is the amount of gas taken up slowly, $A$, a constant, $D$, the diffusion coefficient, $q$, the amount of gas adsorbed on the surface, and $t$, the time.

It may be seen that at 300° and 400° the kinetics of the sorption process agree very well with this equation, while at 70° and 100° the process takes an entirely different course.

In order to calculate the activation energy of the process taking place at 300° to 400° we used the following equation,[2]

$$D_2/D_1 = e^{E/R(1/T_1 - 1/T_2)} \qquad . \qquad . \qquad . \qquad (2)$$

where $D_1$ and $D_2$ are the diffusion coefficients at temperatures $T_1$ and $T_2$ respectively. The results are given in Table I.

TABLE I.

| Expt. No. | Initial Pressure in mm. | $A\sqrt{D}$. | | Activation Energy, $E$ cal./mol. | $E$ as Calculated from Equation (3). |
|---|---|---|---|---|---|
| | | 300°. | 400°. | | |
| 27-28 | 2·36 | 0·0305 | 0·0536 | 8·600 | 7·800 |
| 37-38 | 2·33 | 0·0316 | 0·0549 | 8·400 | 8·100 |
| 41-42 | 1·18 | 0·0226 | 0·0408 | 9·000 | 8·800 |

In order to calculate the heat of activation for the activated adsorption we used the equation suggested by Taylor and Williamson [9]

$$\ln t_1/t_2 = E/R(1/T_1 - 1/T_2) \qquad . \qquad . \qquad . \qquad (3)$$

where $t_1$ and $t_2$ are the time taken to reach a definite value of the volume adsorbed at temperatures $T_1$ and $T_2$ respectively.

The results are given in Table II. Thus the activation energy of the process of activated adsorption is two and a half times as great as that of a process taking place at 300° to 400°.

TABLE II.—THE HEAT OF ACTIVATION. $E$ CAL./MOL.

| Temperature. | Gas Adsorbed in c.c. | | | |
|---|---|---|---|---|
| | 0–0·3. | 0·3–0·5. | 0·5–1·0. | Average 0–1·0. |
| 50-70° | 14·800 | 17·700 | 22·700 | 20·300 |
| 70-100° | — | 19·900 | 20·100 | 20·500 |
| 100-148° | — | — | — | 18·900 |

This, together with the possibility of using the diffusion equation enables us to assume, that the second slow sorption process observed at temperatures above 150° C. cannot be a second type of activated adsorption, but is a process of activated diffusion or solution.

[9] H. Taylor and Williamson, *J. Amer. Chem. Soc.*, 1931, **53**, 2168.

With a value of 20,000 Cals. for the heat of activation of activated adsorption it can be shown, that equilibrium pressure at 300° should already be reached in about $14 \times 10^{-4}$ min., and at 400° to within $0.9 \times 10^{-4}$ of a minute. Thus, we were right in assuming that the kinetic curves at 300° and 400° represent the process of diffusion.

On the other hand, it may be supposed from the same facts, that
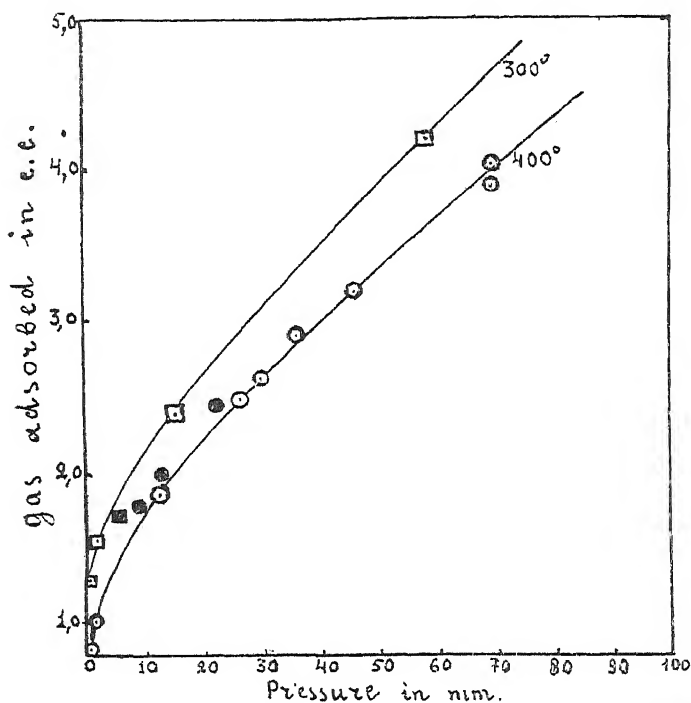


FIG. 5.—Isotherms of activated adsorption of hydrogen on iron. ■ ● — at desorption.

the isotherms for instantaneous sorption at these temperatures should be regarded as the true isotherms for activated adsorption. In Fig. 5 are given the isotherms for temperature of 300° and 400°, the graphs showing that with decreasing pressure the sorption equilibrium is again attained almost instantaneously, i.e., the sorption isotherms are reversible (if, of course, we take into consideration the additional amount of gas taken up irreversibly by diffusion).

TABLE III.

| Volume Adsorbed in c.c. | Equilibrium Pressure in mm. | | Heat of Adsorption. Q Cal./mol. |
|---|---|---|---|
| | 300°. | 400°. | |
| 1·0 | 0·3 | 1·0 | 9·220 |
| 1·25 | 1·15 | 2·8 | 6·820 |
| 1·50 | 2·6 | 6·8 | 6·140 |

The heats of activated adsorption obtained from these isotherms for various amounts of gas adsorbed are given in Table III.

## The Relation between the Activated and the Van der Waals' Adsorption.

If activated adsorption is a surface process, it seems quite natural that it should affect the condition of the surface and thus the amount of the van der Waals' adsorption. It will also be natural to assume that these two types of adsorption should be additive.

It can, however, be seen even from the results obtained by Howard,[6] that this phenomenon is rather more complex.

Howard has shown, that in the case of the sorption of hydrogen by chromium oxide the presence of gas on the surface in an activated form causes a marked decrease in the amount of van der Waals' adsorption. The hydrogen was taken up in the temperature range where the activated adsorption takes place; the catalyst was cooled and pumped off at room temperature. Van der Waals' isotherms were then determined in the ordinary way. The total amount of van der Waals' adsorption diminished enormously, but no simple additivity was to be observed.

The same results have been obtained by us for the sorption of hydrogen on iron (Table IV.).

It may, however, be seen from Table IV. that the problem is further complicated by the following fact. If no pumping off of the gas space was carried out, but the system was brought rapidly to $- 190°$, the additional amount of gas adsorbed corresponded exactly to the normal amount of van der Waals' adsorption at the same final pressure, *i.e.*, the activated adsorption seems to cause no decrease in the amount of van der Waals' adsorption.

TABLE IV.—THE RELATION BETWEEN THE ACTIVATED AND THE VAN DER WAALS' ADSORPTION.

| Activated Adsorption. | | | Van der Waals' Adsorption at $-190°$. | | |
|---|---|---|---|---|---|
| Expt. No. | Temperature. | Gas Adsorbed in c.c. | Equilibr. Pressure in mm. | Normal in c.c. | Observed after Activated Adsorption in c.c. |
| A. With the pumping off a gas space. | | | | | |
| 17 | 400° | 2·46 | 20·0 | 3·1 | 2·45 |
| 19 | 70° | 6·31 | 20·0 | 3·1 | 1·44 |
| B. Without the pumping off a gas space. | | | | | |
| 9 | 0° | 0·192 | 0·747 | 0·500 | 0·560 |
| 18 | 70° | 7·36 | 4·40 | 1·27 | 0·95 |
| 13 | 100° | 5·85 | 5·3 | 1·42 | 1·40 |

This fact cannot, of course, be regarded as a disproof of the surface nature of activated adsorption, for by a modification of the same experiment this superficial nature is confirmed. It rather points to the fact that activated adsorption cannot be considered as a simple covering of the surface of a catalyst. It is a more complex phenomenon and has to be further investigated.

## Summary.

1. Three different types of sorption are shown to exist in the temperature range between $-190°$ and $+400°$ for the sorption of hydrogen by iron. They are : van der Waals' adsorption, activated adsorption, and activated diffusion.

2. In certain temperature ranges it is possible to separate these processes and investigate the kinetics of each individual process.

3. A value of $E \sim 20,000$ Cals. has been obtained for the activation energy of activated adsorption (for a 1·0 c.c. of amount of gas adsorbed) and a value of $E \sim 8,000$ Cals.—for activated diffusion.

4. In the temperature range from $300°$ to $400°$ the activated adsorption is an instantaneous and entirely reversible sorption process. Owing to this the true isotherms of activated adsorption could be obtained and from these the heat of adsorption has been calculated.

5. Howard's results showing that the activated adsorption diminishes the van der Waals' adsorption are confirmed. It is shown, however, that under certain experimental conditions the absence of such a relation between the two types of sorption is possible.

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# INVESTIGATIONS ON THE RADICAL HO₂ IN SOLUTION.

### By Joseph Weiss.

The existence of the radical $HO_2$ was first assumed by Haber[1] in connection with the reaction mechanism of the combustion of hydrogen with oxygen in the gaseous state. More recently Taylor[2] and Bates,[3] and Farkas and Sachsse[4] have also assumed the formation of the radical $HO_2$ from the reaction of hydrogen atoms with oxygen molecules. Harteck[5] has shown that the intermediate formation of $HO_2$ appears to take place in the reaction between hydrogen atoms and oxygen molecules at low temperatures. Recently Bodenstein and Schenck[6] have explained the inhibiting action of oxygen in the reaction between hydrogen and chlorine on the basis of the formation of $HO_2$.

Haber and Willstätter[7] and Haber and Weiss[8] have assumed the formation of the $HO_2$ radical in connection with their work on the catalytic decomposition of hydrogen peroxide in solution. It has been shown that in the homogeneous and heterogeneous[9] decomposition of

[1] *Cf.* F. Haber, *Naturwissenschaften*, 1931, **19,** 450 ; Bonhoeffer and Haber, *Z. physik. Chem.*, 1928, **137A,** 263.

[2] Taylor and Salley, *J. Amer. Chem. Soc.*, 1933, **55,** 96.

[3] Bates, *J. Amer. Chem. Soc.*, 1933, **55,** 426.

[4] L. Farkas and H. Sachsse, *Z. physik. Chem.*, 1934, **27B,** 111.

[5] *Cf.* P. Harteck, *Trans. Farad. Soc.*, 1933, **29,** 134.

[6] Bodenstein and Schenck, *Z. physik Chem.*, 1933, **20B,** 420.

[7] Haber and Willstätter, *Ber.*, 1931, **64,** 2844.

[8] Haber and Weiss, *Proc. Roy. Soc.*, 1934, **147A,** 332.

[9] J. Weiss (*in the press*).

hydrogen peroxide the radicals OH and $OH_2$ play an important rôle, and that often a chain reaction occurs according to the equations :—

$$OH + H_2O_2 = H_2O + HO_2 + 20 \text{ Kcal.}, \qquad . \qquad . \qquad (1)$$
$$HO_2 + H_2O_2 = O_2 + H_2O + OH + 18 \text{ Kcal.} . \qquad . \qquad (2)$$
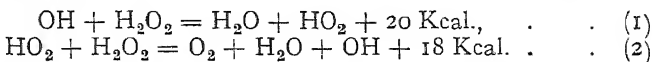
Water and molecular oxygen are formed during this process.

On the other hand, in developing the ideas of Franck and Haber [10] on oxidation processes with molecular oxygen in solutions, it has been deduced that the first reduction product of the $O_2$-molecule is the $O_2^-$-ion. Its connection with the $HO_2$ in aqueous solutions is expressed by the equilibrium :

$$O_2^- + H^+ \rightleftharpoons HO_2.$$
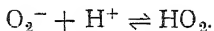
All these investigations certainly indicate a greater probability for the existence of the $HO_2$ radical, but of course they cannot be regarded as a direct proof. However, more direct evidence has recently been obtained by the author during a study of the relation between the radical $HO_2$ and ozone in aqueous solutions. This will now be discussed in detail.

## § 1. Formation of the Radical in Reactions with Molecular Oxygen.

When oxygen is passed over molten potassium at 300° C., potassium peroxide is formed according to the equation :

$$K + O_2 = KO_2.$$
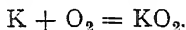
This potassium peroxide may be expressed by the general formula $(KO_2)_n$. M. Traube [11] has assumed that it exists in the form $K_2O_4$, and this view has been generally accepted. Bayer and Villiger [12] have found, on the other hand, that ozone and solid potassium hydroxide also form this orange-red potassium peroxide, which decomposes quickly on the addition of water with the liberation of molecular oxygen. They also ascribe to this peroxide the formula $K_2O_4$, and regard it as the potassium salt of a hypothetical ozonic acid $H_2O_4$; but here again there was no proof of the existence of the $H_2O_4$, or of its potassium salt.

Recently Neuman,[13] who investigated this potassium peroxide at the suggestion of Pauling, has pointed out that the formula $K_2O_4$ would be difficult to understand in many respects. The most reasonable electronic structure for the $O_4^=$-ion would be $: \overset{..}{O} : \overset{..}{O} : \overset{..}{O} : \overset{..}{O} :$, but this compound should be diamagnetic and colourless. It is, in fact, rather highly coloured. Neuman has therefore investigated the magnetic properties of the substance and has found that it actually was paramagnetic with a Bohr magneton number 2·04 at room temperature. This is close to the value 1·73 for the spin moment of an unpaired electron as well as to the value 1·83 of a $^2\pi$-molecule, with doublet separation, as calculated by Van Vleck ; the discrepancy may be due to experimental error, or possibly to mutual interaction of the magnetic dipoles in the condensed phase.

According to this investigation, we have to assume the $O_2^-$-ion, and hence to attribute to the potassium peroxide molecule the formula $KO_2$.

[10] J. Franck and F. Haber, *Sitzungsber. preuss. Akad. Wiss.*, 1931, 250.
[11] Traube, *Ber.* 1912, **45**, 2201, 3319.
[12] Bayer and Villiger, *ibid.*, 1902, **34**, 855.
[13] Neuman, *J. Chem. Physics*, 1934, **2**, 31.

The close relation between ozone and the $HO_2$ radical is now obvious, and can be expressed by the equation :

$$2HO_2 = O_3 + H_2O + 35 \text{ Kcal.} \qquad . \qquad . \qquad . \qquad (3)$$
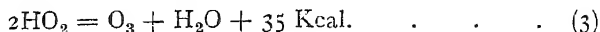
There is no evidence at all for $H_2O_4$ and for its potassium salt, as postulated by the earlier investigators. Rather we have to deal with the radical $HO_2$ and with $KO_2$.

The formation of small amounts of ozone (readily detected by smell) in the decomposition of hydrogen peroxide and some other oxidising agents, under suitable conditions, has previously been mentioned by Schönbein, but so far has remained unexplained. It can now easily be understood by assuming the interaction of $HO_2$ radicals according to reaction (3) during these processes.

In the same way, traces of ozone are formed in certain oxidation processes involving molecular oxygen.[14]

It may perhaps be possible to explain in this way the formation of small amounts of ozone in the assimilation process of plants, as shown by the relatively high ozone concentration present in forests.

According to Willstätter [15] the primary process in the assimilation is given by the equation : Chlorophyll + $O_2$ = Monodehydrochlorophyll + $HO_2$, so that some amount of ozone may be formed as indicated above.

For the direct analytical proof of the formation of ozone from $HO_2$ we have made a few experiments on the basis of analytical determinations of ozone in the presence of hydrogen peroxide, which is also formed to a certain extent.

Rothmund and Burgstaller [16] have worked out a volumetric method for this purpose, but this method was not suitable for our experiments, as it could only be used for determining relatively large concentrations, and, furthermore, does not seem to be accurate enough. We have used a quite different method in which titration and gas volumetric measurements are made simultaneously. The titration of iodine liberated from potassium iodide, or the direct titration with potassium permanganate in acid solution, can be used. In both cases one has to measure simultaneously the oxygen evolved during the titration.

The stoichiometric equations are given as follows :—

*Iodometric Titration.*

(ozone) $\quad O_3 + 2I' + H_2O = O_2 + I_2 + 2OH'$
$\qquad\qquad$ 1 mol $I_2$ . . . 1 mol $O_2$

(hydrogen peroxide) $\quad H_2O_2 + 2I' + 2H^{\cdot} = I_2 + 2H_2O$
$\qquad\qquad$ 1 mol $I_2$ . . . no oxygen.
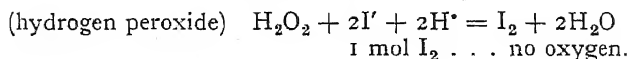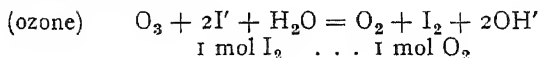
*Permanganate Titration.*

(ozone)
$\quad 2KMnO_4 + 5O_3 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 10O_2$
$\qquad\qquad$ $2KMnO_4$ . . . $10O_2$ mols.

(hydrogen peroxide)
$\quad 2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$
$\qquad\qquad$ $2KMnO_4$ . . . $5O_2$ mols.
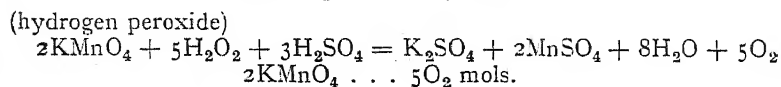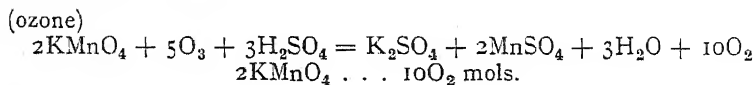
[14] *Cf.* J. Weiss, *Nature*, 1934, **133**, 648; I. Weiss, *Naturwissenschaften*, 1935, **23**, 69.
[15] Willstätter, *Naturwiss.*, 1933, **21**, 252.
[16] Rothmund and Burgstaller, *Monatshefte Chem.*, 1913, **34**, 693.

In using potassium permanganate, it is obvious that with ozone twice as much oxygen is liberated as with hydrogen peroxide, while with iodine ions the oxygen liberated accounts completely for the ozone.

Let us denote by $C_s$ the total amount of the titrating agent potassium permanganate required for a certain sample, and by $g$ the total oxygen evolved during the reaction. Let the number of c.c. of oxygen liberated by 1 c.c. of the titrating agent in the case of pure hydrogen peroxide under the same conditions be $v$. Then the values of the titrating agent needed for the ozone $(C_{O_2})$ and for the hydrogen peroxide $(C_{H_2O_2})$ are given respectively by

$$C_{O_3} = g/v - C_s, \qquad C_{H_2O_2} = 2C_s - g/v.$$

The method with permanganate was first used by Bach [17] for a similar problem. However, Bach did not interpret his results in a correct way. In the original experiments a Wolff bottle was used, but the method becomes more accurate if efficient shaking is provided. The simple apparatus is shown in Fig. 1. The vessel is filled with the solution to be investigated and connected to a gas burette. In a small dish, $d$, in the vessel we have a measured excess of $KMnO_4$ solution. The small dish is then inverted by turning the stop-cock and whilst shaking, the oxygen evolved is collected. The excess permanganate is afterwards titrated with acid $FeSO_4$ solution. Greater accuracy is obtained if the vessel is placed in a thermostat.
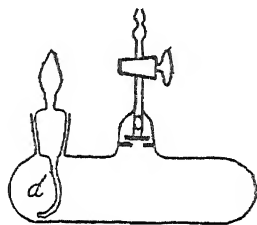


FIG. 1.

The important experiments made by Bach, using palladium hydride, have been repeated, and we have been able to confirm his results. Palladium sheets saturated with hydrogen were added to 20 c.c. $n$-$H_2SO_4$ in a small bulb. Oxygen was then bubbled through the liquid for 1 to 2 hours, the temperature being maintained at about 5 to 7° C. The liquid was then rapidly removed from the palladium and analysed by the method described above. The values obtained from a series of experiments showed that the liberated oxygen was on the average 10 per cent. in excess of that calculated for pure hydrogen peroxide. It follows therefore that from the total consumption of potassium permanganate about 1/10 was needed for ozone and about 9/10 for the hydrogen peroxide present.

Owing to the very small concentrations with which we are dealing, the mean experimental error may be estimated as relatively high ($\pm$ 30 per cent.). However, the results appear to be quite definite from a qualitative point of view, and are of particular interest, since we are able to investigate the reaction between hydrogen atoms and molecular oxygen at room temperature.

The recent work of Franck [18] and other investigators has shown that hydrogen atoms are present on the surface of palladium saturated with hydrogen gas. The reaction with molecular oxygen could then be expressed by the following equations :

$$H + O_2(+ M) = HO_2(+M) + 45 \text{ Kcal.} \qquad . \qquad . \quad (4)$$
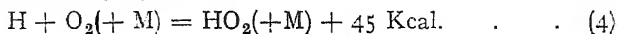
Here again the primary process is the formation of $HO_2$, as has already been assumed in the gas phase reaction. The $HO_2$ can give ozone as indicated in reaction (3) above, or hydrogen peroxide according to :

$$2HO_2 = H_2O_2 + O_2 + 49 \text{ Kcal.,} \qquad . \qquad . \quad (5)$$
$$HO_2 + H = H_2O_2 + 94 \text{ Kcal.} \qquad . \qquad . \quad (6)$$
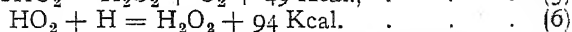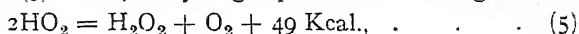
[17] Bach, *Ber.*, 1900, **33**, 1506.          [18] J. Franck, *Nachr. Göttinger Ges.*, 1933.

It seems reasonable to suppose that the well-known formation of ozone in the hydrogen flame is also mainly due to this reaction (3).

In the above equation (4) the value 45 kilocal. has been taken as the energy for the addition of the first H-atom to an $O_2$-molecule.

Bodenstein and Schenck,[6] from a study of the inhibition of the $H_2$—$Cl_2$—reaction by molecular oxygen, have estimated this energy to have a value of about 44 kilocalories, whilst Haber and Weiss [8] have found a value $\sim 50$ kilocal. for this energy from the catalytic decomposition of hydrogen peroxide by ferric salts.

From quantum mechanical considerations, Heitler [19] has shown that reaction (6) is more exothermic than reaction (4), in agreement with experiment. He gives a provisional value for the energy of addition of the first hydrogen atom about 60 kilocal.

Another series of experiments was carried out with potassium and sodium superoxides. These superoxides were decomposed with sulphuric acid at about 5-7° C. $HO_2$ is formed according to the stoichiometric equation :

$$KO_2 + H_2SO_4 = KHSO_4 + HO_2.$$
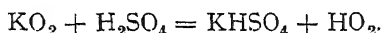
The $HO_2$ gives here again ozone and hydrogen peroxide according to reactions (3) and (5).

The resulting acid solutions were analysed as before, and gave the following results (mean of three experiments) :—

| Substance. | Per Cent. Excess Liberation of Oxygen. | Per Cent. Ozone. |
|---|---|---|
| Sodium peroxide (commercial) | 17 | 20·5 |
| Potassium peroxide | 28 | 39 |

In these latter cases a higher percentage of ozone might be expected, but the relatively low values obtained can readily be understood if we consider that the $HO_2$ is also taking part in the reaction (2) with hydrogen peroxide and in the reaction (8) with ozone. These reactions will be discussed later.

So far, we have dealt mainly with the formation of ozone from $HO_2$ radicals. It is obvious that also the reverse process must take place to a certain extent. Actually, it can be shown that under certain conditions such a process does occur even with a considerable velocity. Evidence of this can be seen from the fact that the above-mentioned $KO_2$ can also be prepared by passing ozone into a concentrated solution (40 per cent.) of KOH in water at low temperatures, as has been observed by Bayer and Villiger.[12] Their interpretation of the results is, however, not quite correct.

## § 2. Spectroscopic Investigations of Ozone in Aqueous Solutions.*

We have attempted to determine whether ozone undergoes any marked change in aqueous or dilute acid or alkaline solution. For this purpose a spectroscopic investigation of aqueous ozone solutions has been made. Ozonised oxygen was bubbled through a suitable solution con-

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[19] *Private Communication.*

* I am very grateful to Dr. L. Farkas for his most valuable advice during these spectroscopic investigations.
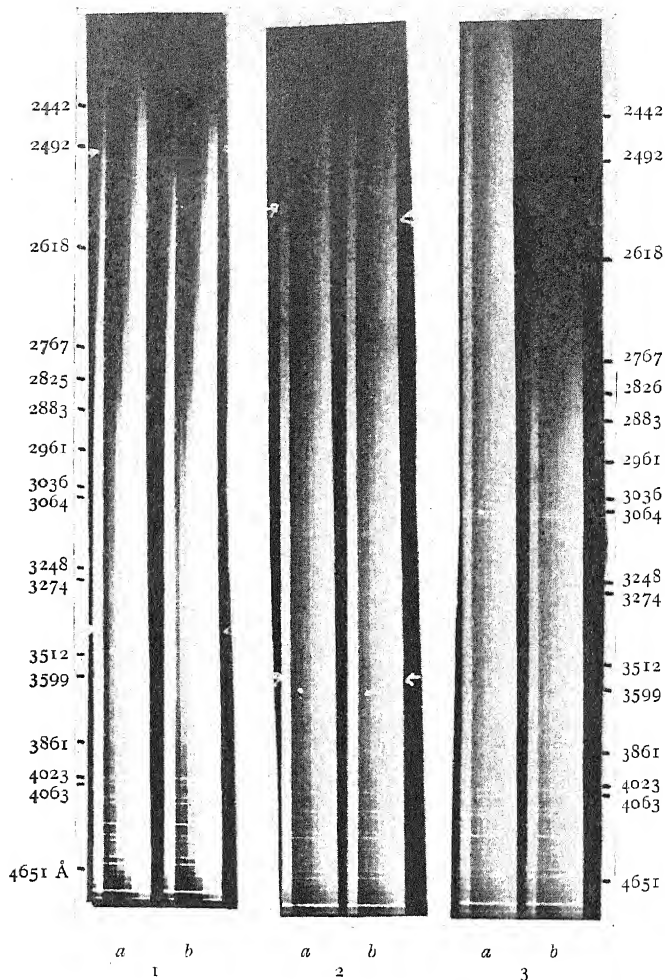
## FIG. 2.

1a. 1 m. KOH (− 3° C.).
  b. 1 m. KOH, 0·9 . 10⁻⁴ mols. $O_3/l$ (− 3° C.).
2a. 7·15 m. KOH (− 30° C.).
  b. 7·15 m. KOH, 1·5 . 10⁻³ mols. $O_3/l$ (− 30° C.).
3a. 10⁻² m. $H_2SO_4$ (−0·2° C.).
  b. 10⁻² m. $H_2SO_4$, 1·4 . 10⁻⁴ mols. $O_3/l$ (− 0·2° C.).
4a. 7·15 m. KOH (− 40° C.).
  b. 7·15 m. KOH, 0·6 . 10⁻³ mols. $O_3/l$ (− 40° C.).
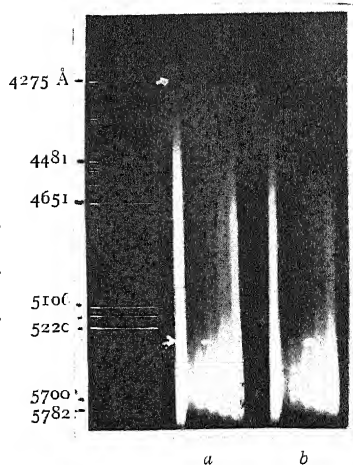
tained in a quartz cell. In all cases the quartz cell was cooled to prevent considerable decomposition of the ozone in the aqueous solution during the experiment. One series of experiments was made with dilute aqueous solutions at about $0°$ ( $\pm$ $1°$) C., and another series with 40 per cent. KOH solutions at $- 20°$ to $- 40°$ C. In the latter case the cell was surrounded with the cooling mixture in a quartz Dewar vessel with windows.

After having taken the photograph the contents of the cell were analysed to determine the amount of ozone. A hydrogen lamp (3 amps.) was used for the ultra-violet and an Osram " Bandlampe " (13 amps.) for the visible region of the spectrum. The photographs were taken using a Zeiss " Stufenfilter " in order that qualitative photometric measurements might be made. A detailed description of the experiments and some calculations will be published shortly. Only the more qualitative results will be discussed here (Fig. 2).

Gaseous ozone has, as is well-known, quite a strong absorption in the ultra-violet, with a maximum at 2550 Å. The main features of the spectrum of gaseous ozone are also found in spectra of acid solutions of ozone. The spectrum in the latter case has a more diffuse character, which may perhaps be attributed to slight hydration as the ozone molecule has most probably a dipole moment. But if we study pure aqueous solutions and increasingly alkaline solutions, it is found that the absorption in the ultra-violet decreases, and finally practically disappears in stronger alkaline solutions. In highly concentrated alkaline solutions (40 per cent. KOH) at low temperatures ($- 40°$ C.), we get absorption in the blue region of the visible, due presumably to $KO_2$ and $O_2^-$-ion.[**]

We find the chemical behaviour of these aqueous ozone solutions in complete agreement with the result of the spectroscopic investigation. It is well known that one can prepare stable solutions of ozone in certain organic solvents such as $CHCl_3$ and $CCl_4$. The rate of decomposition of ozone in these solutions is not very different from that in the gaseous phase, even though the mechanism may be modified by the presence of solvent molecules.[20] We have therefore strong evidence to assume that the ozone exists as $O_3$ molecule in these solutions. Strongly acid solutions also show chemical and physical properties similar to gaseous ozone. For example, Henry's law holds in a very good approximation.[21] But this is not so in the case of weakly acid or alkaline solutions. These solutions have quite different properties, and show a rate of decomposition which is, even in neutral aqueous solutions, at least $10^4$ times greater than in the gaseous phase.[22]

All these experimental facts can be easily understood on the assumption of formation of $HO_2$, according to the equation

$$O_3 + OH^- \rightarrow O_2^- + HO_2. \qquad . \qquad . \qquad . \qquad (7)$$
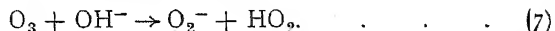
## § 3. The Decomposition of Ozone in Aqueous Solutions.

The decomposition of ozone in aqueous solutions, catalysed by $OH^-$ ions, can now easily be treated on a quantitative basis. The primary process (7) shown above, may be followed by the chain reactions :

$$O_3 + HO_2 = 2O_2 + OH + 33 \text{ Kcal.,} \qquad . \qquad . \qquad (8)$$
$$O_3 + OH = O_2 + HO_2 + 34 \text{ Kcal.,} \qquad . \qquad . \qquad (9)$$
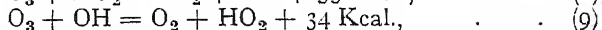
[**] It might be possible to estimate from this a value for the electron affinity of the oxygen molecule. This point will be discussed in a later paper.

[20] Bowen, Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.* 1931, **137**A, 211.
[21] Rothmund and Burgstaller, *Nernst-Festschr.*, 1912, 391.
[22] E. Warburg, *Ann. Physik*, 1902, (4), **9**, 1286.

which is similar to the hydrogen peroxide chain reaction in some respects. The energies can be calculated from known data.

We have further to take into account the above discussed reaction (3) which gives ozone by the interaction of two $HO_2$ radicals.

Also the reaction

$$HO_2 + OH = O_2 + H_2O + 70 \text{ Kcal.,} \qquad . \qquad . \quad (10)$$
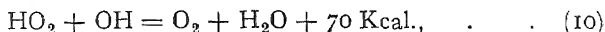
which seems to play an important part in the photochemical decomposition of hydrogen peroxide,[8] must be considered.

Taking into account both these chain breaking processes (reaction 3 and 10) it is not possible in practice to make a complete calculation of the reaction velocity. It is, however, possible to deduce some information concerning the course of the reaction by treating it separately with respect to reaction (3) and (10).

The calculation of the reaction velocity in the stationary state has been made by putting

$$\frac{d(OH)}{dt} = 0, \qquad \frac{d(HO_2)}{dt} = 0.$$

If we introduce the reaction (3) into the calculation (which is only essential when dealing with small ozone concentrations), we obtain for the rate of decomposition the equation :

$$-\frac{d(O_3)}{dt} = \frac{2}{3}\frac{d(O_2)}{dt} = 2k_3\sqrt{\frac{2k_7}{k_9}}[O_3]^{\frac{3}{2}}[OH^-]^{\frac{1}{2}} \qquad . \qquad . \quad (\alpha)$$

By taking reaction (10) into account, we obtain the more complicated relationship :

$$-\frac{d(O_3)}{dt} = \frac{2}{3}\frac{d(O_2)}{dt} = \frac{2}{3}k_7[O_3][OH^-] + \frac{k_3}{3}[O_3][OH^-]\left\{\sqrt{1 + \frac{4k_7k_8[O_3]}{k_3k_{10}[OH^-]}} - 1\right\}$$
$$+ \frac{8}{3}\frac{k_7k_8}{k_{10}}\frac{[O_3]^2}{\left\{\sqrt{1 + \frac{4k_7k_8[O_3]}{k_3k_{10}[OH^-]}} - 1\right\}} \qquad . \quad (\beta)$$

If we assume there that the second term under the square root sign is large compared with 1, we get the following formula :

$$-\frac{d(O_3)}{dt} = \frac{2}{3}k_7[O_3][OH^-] + 2\sqrt{\frac{k_3k_7k_8}{k_{10}}}[O_3]^{\frac{3}{2}}[OH^-]^{\frac{1}{2}}. \qquad . \quad (\gamma)$$

It will be seen that the second term here is very similar to equation ($\alpha$). It is, of course, practically impossible to calculate the reaction velocity with such a complicated relation as equation ($\beta$), as it would also involve the use of too many arbitrary constants. Equation ($\gamma$) will be used instead as it may be regarded in any case as a good approximation.

Two detailed experimental investigations have been carried out on the decomposition of ozone in aqueous solution. Previous work has been done by Rothmund and Burgstaller,[23] who investigated the decomposition of ozone at 0° C. in weak sulphuric and nitric acid solution in the concentration range of $10^{-4}$ to $10^{-2}$ equivalents per litre. They have found that over this concentration range the velocity is independent of the nature of the acid, the change in the rate being due only to the

[23] Rothmund and Burgstaller, *Monatshefte f. Chem.*, 1913, **34**, 668. (*Akad. d. Wissensch.*, *Wien*.

difference in the hydrogen-ion concentration. The rate of decomposition increases with falling acidity, but a relationship much less than linear is obtained.

The results obtained by Rothmund and Burgstaller for acid solutions are shown in Table I. The second order constants ($K_{\text{bim.}}$), as calculated by previous investigators, are given, and in addition, we have calculated the $3/2$ order constants according to equations ($\alpha$) and ($\gamma$). These latter constants are at least in as good agreement as those calculated for a bimecular reaction.

TABLE I.

| No. | Experiment. | Time $t$ in Minutes. | Concentration $[O_3] \cdot 10^3$ mols./lr. | $K \cdot 10^3$ (3/2 order). | $K_{\text{bimolecular.}}$ |
|---|---|---|---|---|---|
| 1 | 0·01 $H_2SO_4$ 0° C. | 0 | 1·600 | — | — |
| | | 342 | 1·478 | 6·43 | 0·151 |
| | | 1292 | 1·293 | 4·33 | 0·115 |
| | | 1758 | 1·200 | 4·44 | 0·118 |
| | | 2763 | 1·061 | 4·20 | 0·115 |
| | | | mean value $K_{(1)} = 4.86$ | | |
| 2 | 0·0005 $H_2SO_4$ 0° C. | 0 | 0·781 | — | — |
| | | 261 | 0·695 | 16·6 | 0·607 |
| | | 1371 | 0·483 | 14·3 | 0·576 |
| | | 2701 | 0·319 | 15·0 | 0·686 |
| | | 4187 | 0·250 | 13·2 | 0·645 |
| | | | mean value $K_{(2)} = 14.80$ | | |
| 3 | 0·0001 $H_2SO_4$ 0° C. | 0 | 0·686 | — | — |
| | | 30 | 0·678 | 16·7 | 0·573 |
| | | 184 | 0·633 | 16·8 | 0·663 |
| | | 329 | 0·606 | 15·2 | 0·585 |
| | | 1300 | 0·421 | 16·2 | 0·707 |
| | | 1760 | 0·349 | 17·4 | 0·800 |
| | | 2760 | 0·258 | 17·5 | 0·876 |
| | | | mean value $K_{(3)} = 16.6$ | | |

The ratio of the mean values of the velocity constants in 0·01 $n$ $n$-$H_2SO_4$ ($K_{(1)}$) and in 0·0005 $n$-$H_2SO_4$ ($K_{(2)}$) solution :

$$\frac{K_{(1)}}{K_{(2)}} = \frac{14\cdot4}{4\cdot86} \sim 3$$

is found experimentally to have very approximately the same value as the ratio

$$\sqrt{\frac{[H^\cdot]_{(1)}}{[H^\cdot]_{(2)}}} = \sqrt{\frac{10^{-2}}{5 \times 10^{-4}}} \sim 4\cdot5.$$

Although the agreement is not very close, it indicates that we can hardly assume more than a square root relationship with the OH' concentration, a fact which also follows from the uniform $3/2$ order constants.

Recently Sennewald [24] has investigated the decomposition of ozone in aqueous solution in which the $p_H$ was varied over a range 5·3 to 8 by means of buffer solutions. He assumes the reaction to be bimolecular with respect to the ozone. We have, however, calculated the constants

[24] Sennewald, *Z. physik. Chem.*, 1933, 164A, 305.

on the basis of a 3/2 order reaction, and find that they agree quite as well as the bimolecular constants. The values are shown in Table II.

TABLE II.

| No. | Experiment. | Concentration [O$_3$] . 10$^3$ mols./lr. | Half Time Period in Minutes. | $K$ (3/2 order). | $K_{bimolecular}$. |
|-----|-------------|------------------------------------------|------------------------------|------------------|---------------------|
| 1 | $p_H = 5\cdot29$ 0° C. | 1·25 | 78 | 2·12 | 10·3 |
|   |             | 1·00 | 91 | 2·04 | 11·0 |
|   |             | 0·750 | 105 | 2·10 | 12·7 |
|   |             | 0·500 | 125 | 2·10 | 16·0 |
| 2 | $p_H = 6\cdot00$ 0° C. | 1·25 | 64 | 2·59 | 12·5 |
|   |             | 1·00 | 80 | 2·32 | 12·5 |
|   |             | 0·750 | 105 | 2·10 | 12·7 |
|   |             | 0·500 | 125 | 2·10 | 16·0 |

After making certain corrections for the influence of the buffer solution salts Sennewald was able to represent the dependence of the velocity constants on the OH$^-$ concentration by a relation of the form :

$$K = \text{prop} \ [OH^-]^{0\cdot36}.$$

Here, again, it will be seen that over the fairly acid range, the velocity does not in any instance depend upon the OH$^-$ concentration to a greater extent than with the square root.

Rothmund and Burgstaller [16] have also carried out some experiments, using slightly alkaline solutions of ozone. The experimental accuracy even in the investigations in acid solutions was not very great, but in the case of alkaline solutions was considerably less owing to the much smaller ozone concentrations which had to be used.

These previous investigators have already observed that in alkaline solution a reaction of the first order with respect to the ozone becomes prominent, and is sensitive to $p_H$ to a much greater extent than the reaction in acid solution. It will be seen from our equation $(\gamma)$ that at higher OH$^-$-ion concentration the first term, which is proportional to OH$^-$ and first order with respect to ozone, becomes important.

Taking into account all the experimental facts available at present, formula $(\gamma)$ may be regarded as a good first approximation.

## § 4. The Reaction between Ozone and Hydrogen Peroxide.

But there is still another important point in the decomposition of aqueous ozone solutions which has not yet been mentioned ; it is the accelerating influence of hydrogen peroxide.

If we determine in an aqueous solution of ozone and hydrogen peroxide the mean consumption ratio

$$\bar{n} = \frac{\text{mols. ozone decomposed}}{\text{mols. hydrogen peroxide decomposed}} = \frac{\Delta(O_3)}{\Delta(H_2O_2)}$$

(in the same time interval) during the course of the reaction, we find this ratio not to be unity in all cases, as would be expected from a simple interaction according to the equation

$$O_3 + H_2O_2 = 2O_2 + H_2O.$$

We find that this ratio is often considerably dependent in some way upon the concentration of both the reactants.

Brodie [25] and Schöne [26] who first studied the reaction between ozone and hydrogen peroxide, have actually found a consumption ratio

$$\frac{\Delta(O_3)}{\Delta(H_2O_2)} \sim 1.$$

Rothmund and Burgstaller [27] have made a very close investigation of this reaction. They were able to confirm the results of Brodie and Schöne under the conditions of small ozone concentrations and relatively large hydrogen peroxide concentrations. However, in the case of small $H_2O_2$-concentrations they found much greater values than unity. The highest value which they obtained under their experimental conditions

was $\dfrac{\Delta(O_3)}{\Delta(H_2O_2)} \sim 21.$

Without any detailed discussion, we may conclude from all our previous experience that we are dealing here with a chain reaction, and that it seems to be impossible to represent the complete course of this reaction simply by stoichiometric equations. The value $n = 1$ is then obviously a limiting value due to extreme conditions.

According to our previous investigations, we have actually only one possibility in correlating the decomposition of ozone with the catalytic decomposition of hydrogen peroxide, where also the radicals OH and $HO_2$ occur.

Thus, by taking into account reactions (1) and (2), we should get a complete mechanism for the reaction between $O_3$ and $H_2O_2$.

Calculations have been made for the stationary state by equating to zero the differential quotients with respect to time of the radicals OH and $HO_2$.

As we are mainly interested here in the ratio $\dfrac{d(O_3)}{d(H_2O_2)}$, and not in the rate of the reaction, we may simplify the calculation somewhat.

In calculating the stationary concentration of the OH-radical, we obtain an expression which has the form :

$$[OH] = \frac{k_7[O_3][OH^-]}{2(k_8[O_3] + k_1[H_2O_2])} \left\{ \sqrt{1 + \frac{4(k_9[O_3] + k_2[H_2O_2])(k_8[O_3] + k_1[H_2O_2])}{k_7 k_{10}[O_3][OH^-]}} - 1 \right\}.$$

This has a maximum value when the second term under the square root sign is great compared with 1. We obtain for this case the formula :

$$[OH] = \sqrt{\frac{k_9[O_3] + k_2[H_2O_2]}{k_8[O_3] + k_1[H_2O_2]}} \cdot \frac{k_7}{k_{10}}[O_3][OH^-] = \Psi \sqrt{\frac{k_7}{k_{10}}[O_3][OH^-]},$$

whereby 

$$\Psi = \sqrt{\frac{k_9\dfrac{[O_3]}{[H_2O_2]} + k_2}{k_8\dfrac{[O_3]}{[H_2O_2]} + k_1}}.$$

The same can be done for the radical $HO_2$.

[25] Brodie, *Phil. Trans.*, 1872, **162**, 454.
[26] Schöne, *Liebig Ann.*, 1879, **196**, 239.
[27] Rothmund and Burgstaller, *Monatshefte f. Chem.*, 1917, **38**, 159.

We then obtain for the ratio $n$ (at any moment) the equation :

$$n = \frac{d(O_3)}{d(H_2O_2)} = \frac{k_7[O_3]^{\frac{1}{2}}[OH^-] + \frac{[O_3]}{[H_2O_2]}\left\{k_9\frac{1}{\Psi} + k_8\Psi\right\}}{k_1\Psi + k_2\frac{1}{\Psi}} \quad . \quad (\delta)$$

TABLE III.

| Experiment. | Time $t$ in Minutes. | Concentration $[O_3] . 10^3$ mols./lr. | Concentration $[H_2O_2] . 10^3$ mols./lr. | Mean Consumption Ratio $\bar{n} = \frac{\Delta(O_3)}{\Delta(H_2O_2)}$. | Mean Ratio of the Concentrations $v_m = \frac{[O_3]}{[H_2O_2]}$. |
|---|---|---|---|---|---|
| b | 0 | 1·77 | 0·400 | — | — |
|   | 5 | 1·58 | 0·384 | — | — |
|   | 14 | 1·32 | 0·372 | 21·6 | 3·825 |
|   | 24 | 1·005 | 0·363 | 20·8 | 3·155 |
|   | 39 | 0·630 | 0·330 | 16·3 | 2·338 |
|   | 56 | 0·407 | 0·302 | 13·9 | 1·629 |
| a | 0 | 1·50 | 0·785 | — | — |
|   | 6 | 1·00 | 0·720 | 7·7 | 1·65 |
|   | 14 | 0·510 | 0·660 | 7·9 | 1·08 |
|   | 22 | 0·350 | 0·625 | 7·2 | 0·666 |
|   | 30 | 0·205 | 0·505 | 6·8 | 0·483 |
|   | 45 | 0·108 | 0·545 | 5·8 | 0·302 |
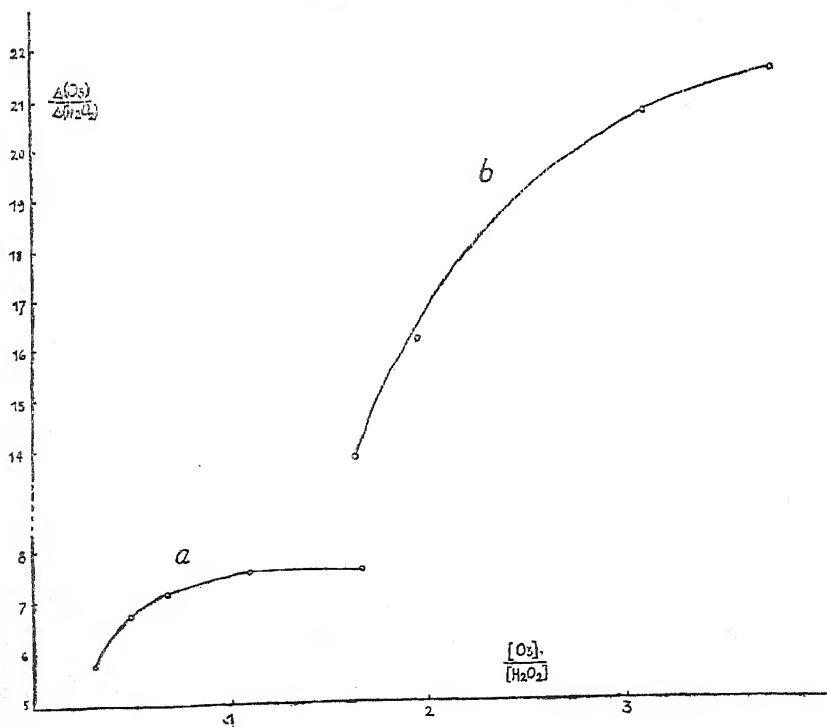


FIG. 3.

The most remarkable fact that we observe from this equation is that the consumption ratio $n$ is not only dependent on the ratio of the concentrations $\dfrac{[O_3]}{[H_2O_2]}$ at every instant, but also depends on an expression of the form $\sim [O_3]^{\frac{1}{2}}[OH^-]$, which naturally cannot be neglected in the case of higher ozone and $OH^-$ concentrations.

In Table III. (experiments $a$ and $b$) are given the data obtained by Rothmund and Burgstaller [16] for two experiments. In Fig. 3 we have plotted the mean consumption values $\bar{n} = \dfrac{\Delta(O_3)}{\Delta(H_2O_2)}$ against the corresponding mean values of the concentrations $\left(\dfrac{[O_3]}{[H_2O_2]}\right)$. It will be seen that smooth curves are obtained, and that even for the same ratio of the concentrations we get different values for $\bar{n}$ for different ozone concentrations, as is predicted by formula ($\delta$).

With increasing $H_2O_2$ concentrations the above formula might take the form :

$$ n = \frac{d(O_3)}{d(H_2O_2)} = \frac{[O_3]}{[H_2O_2]}\left\{\frac{k_8}{2k_2} + \frac{k_9}{2k_1}\right\} + \frac{k_3}{2}[OH^-]\sqrt{\frac{[O_3]}{k_1 k_2}}. \qquad (\epsilon) $$

In this case we should expect a more or less linear relationship between $n$ and the ratio of the concentrations of the reactants. It will be seen that this is the case for the conditions prevailing during the experiment given in Table IV. and Fig. 4.

If the ozone concentration is now decreased, it is no longer possible to neglect the interaction of $HO_2$ radicals (reaction 3) giving ozone.

In order to make calculation possible now, it will be necessary to neglect another reaction as, for example, reaction (9). This would appear to be justifiable, since at high hydrogen peroxide concentrations the OH-radical will mainly react according to reactions (1) and (10).
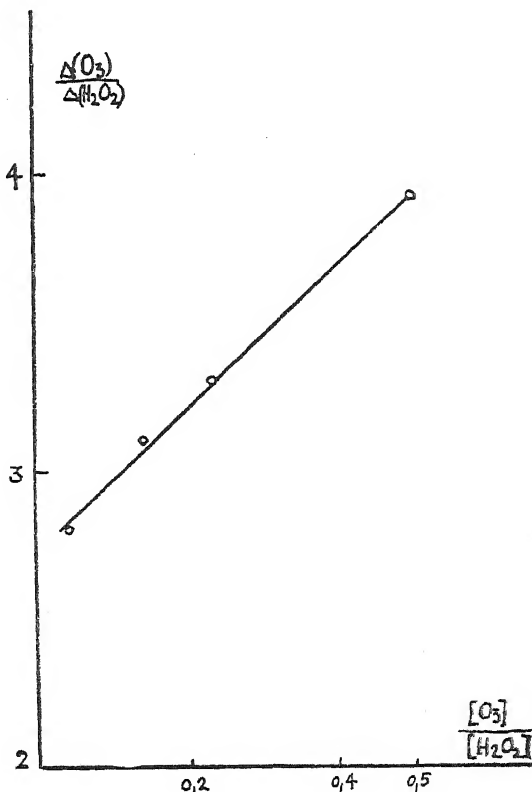


FIG. 4.

TABLE IV.

| Time $t$ in Minutes. | Concentration $[O_3] \cdot 10^3$ mols./lr. | Concentration $[H_2O_2] \cdot 10^3$ mols./lr. | Mean Consumption Ratio $\bar{n} = \dfrac{\Delta(O_3)}{\Delta(H_2O_2)}$. | Mean Ratio of the Concentrations $v_m = \dfrac{[O_3]}{[H_2O_2]}$. |
|---|---|---|---|---|
| 0 | 1·080 | 1·690 | — | — |
| 6 | 0·460 | 1·530 | 3·9 | 0·469 |
| 13 | 0·250 | 1·440 | 3·3 | 0·236 |
| 20 | 0·135 | 1·390 | 3·1 | 0·135 |
| 29 | 0·070 | 1·320 | 2·7 | 0·075 |
| 39 | 0·045 | 1·320 | 2·8 | 0·044 |

We then obtain for $n$ the simple expression :

$$n = \frac{d(O_3)}{d(H_2O_2)} = \frac{[O_3]}{[H_2O_2]} \frac{k_8}{2k_2} + 1. \quad . \quad . \quad . \quad (\eta)$$

It is of interest to note that the second term now becomes unity, owing to the formation of ozone according to reaction (3). In the case of sufficiently small $\dfrac{[O_3]}{[H_2O_2]}$ ratios we obtain

$$n = \frac{d(O_3)}{d(H_2O_2)} \sim \frac{\Delta(O_3)}{\Delta(H_2O_2)} \sim 1.$$

This is in agreement with the experiments of Brodie [25] and Schöne [26] mentioned above. This consumption ratio 1 actually corresponds to extreme conditions, namely small absolute values of ozone concentration and small $\dfrac{[O_3]}{[H_2O_2]}$ ratios, as used by these investigators.

We are further able to make a rough estimate for the limit of the ratio of the constants $\dfrac{k_8}{k_2}$.

The experimental error in Brodie's and Schöne's results was of the order of about $\pm$ 10 per cent. The ratio of the concentrations $\dfrac{[O_3]}{[H_2O_2]}$ present in their experiments can be estimated from the papers of Schöne to be $\sim \frac{1}{100}$.

Therefore we have

$$2\frac{k_8}{k_2}10^{-2} \leqq 10^{-1}, \qquad \frac{k_8}{k_2} \sim \leqq 5.$$

This indicates that the reaction (2) of $H_2O_2$ with the HO$_2$ radical proceeds at least about five times more slowly than the reaction (8) of HO$_2$ with ozone. This fact may perhaps be understood qualitatively, since we are here dealing with similar reactions, but in the case of the conversion of $H_2O_2$ into $H_2O$ a more complicated rearrangement of the atoms process takes place than in the case of ozone giving an $O_2$ molecule.

## Summary.

In solution the radical HO$_2$ has previously been assumed in the catalytic decomposition of hydrogen peroxide and in oxidation processes with molecular oxygen.

It can be shown that this radical stands in a close relation to ozone, as expressed by the equation :

$$2HO_2 = O_3 + H_2O + 35 \text{ Kcal.}$$
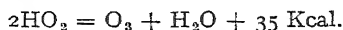
This reaction has been proved for different cases, where the formation of the radical $HO_2$ is to be expected according to the theory.

The inverse reaction is strongly catalysed by hydroxyl ions according to

$$O_3 + OH^- = HO_2 + O_2^-, \qquad (O_2^- + H^+ \rightleftharpoons HO_2).$$
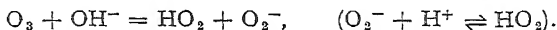
This reaction accounts for the spectroscopic and chemical behaviour of aqueous ozone solutions which have been investigated in detail.

It is further possible to explain quantitatively on this basis the decomposition of ozone in aqueous solution and the reaction between ozone and hydrogen peroxide. In these cases the ozone generally is decomposed in a chain mechanism according to the equations :

$$O_3 + OH = O_2 + HO_2 + 34 \text{ Kcal.},$$
$$O_3 + HO_2 = 2O_2 + OH + 33 \text{ Kcal.}$$
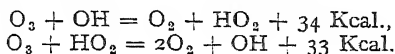
The author wishes to thank Professor F. G. Donnan, F.R.S., for his continuous interest in this work, and the Academic Assistance Council for a financial grant.

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      *University College,*
         *London, W.C. 1.*

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# A THERMODYNAMIC STUDY OF SYSTEMS OF THE TYPE PbCl₂—RCl—H₂O AT 25° C. PART III.

BY MISS D. M. BRASHER AND H. N. PARTON.

A number of investigations have been carried out on the three systems $PbCl_2$—$KCl$—$H_2O$, $PbCl_2$—$NaCl$—$H_2O$, and $PbCl_2$—$LiCl$—$H_2O$, involving measurements of solubility and of activities of the components by E.M.F. and vapour pressure methods.

Parts I.[1] and II.[2] of this series record the study of the system $PbCl_2$—$KCl$—$H_2O$ by Allmand and Burrage, in which the activity of the lead chloride was found by means of the cell

$$\text{Pb / KCl + PbCl}_2 \text{ / AgCl / Ag.}$$
$$\text{aqueous}$$
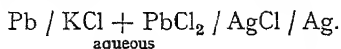
Burrage[3] studied the equilibria in the saturated solutions by solubility determinations. Hunter (unpublished) calculated the activity of water in the system from vapour pressure measurements, and by combination of his results with those of Allmand and Burrage, found the activity of potassium chloride also.

[1] Allmand and Burrage, *Trans. Faraday Soc.*, 1927, **23**, 470.
[2] *Ibid.*, 1933, **29**, 679.          [3] Burrage, *J.C.S.*, 1926, **129**, 1703.

The solubility determinations for the systems containing sodium and lithium chlorides were carried out by Deacon.[4]   One of us (D. M. B.) investigated the system $PbCl_2$—NaCl—$H_2O$ by the E.M.F. method of Allmand and Burrage, using the cell

$$\text{Pb / } PbCl_2 + \underset{\text{aqueous}}{\text{NaCl}} \text{ / AgCl / Ag.}$$
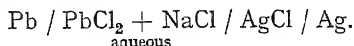
At high concentrations of sodium chloride, the silver chloride was dissolved from the electrodes and irregular results were obtained.   The second author (H. N. P.) has extended the work into the high concentration region up to solutions saturated with both components, using a chlorine electrode.

## Experimental.

**Lead Electrode.**—Amalgamated rods (D. M. B.) and saturated liquid amalgams (H. N. P.) were both used, and gave identical results : 6 per cent. amalgams were prepared from Kahlbaum's pure lead sticks and hot mercury, filtered and stored under nitrogen.

**Silver Chloride Electrodes** were made as described by Allmand and Hunter,[5] and were reproducible to o·1 mv.

**Chlorine Electrode.**—Mixtures of chlorine and nitrogen in contact with platinum-iridium electrodes were used.   Lewis and Rupert [6] showed that mixtures of air and chlorine containing from o·3 per cent. to 5 per cent. of the latter overcame the difficulties found by Muller [7] with pure chlorine due to the reactions

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl'$$

and        $$Cl_2 + Cl' \rightleftharpoons Cl_3'.$$
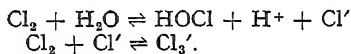
In solutions of high chloride ion concentration, the second reaction would be likely to affect the interpretation of the results, so mixtures dilute with respect to chlorine were required.

A mixture containing about 2·4 per cent. of chlorine was produced by passing nitrogen through liquid chlorine kept at the temperature of melting toluene (− 94·5° C.), at which the vapour pressure of chlorine is 18·5 mm. Hg. It was found possible to produce a continuous stream of the gas mixture of constant composition by this means.   The chlorine electrode was standardised against a number of silver chloride electrodes at different times in the course of the work, the mean value being 1·0840 ± ·0002 volts. This value checked excellently with measurements on the cell

$$\underset{\substack{\text{Satd.}\\\text{amalgam}}}{\text{Pb}} \quad \text{/ } PbCl_2 \text{ satd. / } Cl_2 + \text{RCl}$$
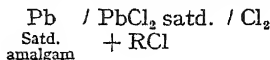
the mean of eight such cells with different amounts of added chloride being 1·5681 ± ·00025 volts.   The difference between these values is 0·4841 volts agreeing well with the value 0·4842 volts for the cell

$$\underset{\substack{\text{Satd.}\\\text{amalgam}}}{\text{Pb}} \quad \text{/ } \underset{\text{Satd.}}{PbCl_2} \text{ / AgCl / Ag.}$$
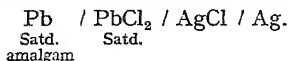
found in the present work and also by Carmody.[8]

**Materials.**

**Lead Chloride** was purified by recrystallisation from dilute hydrochloric acid.

[4] Deacon, *J.C.S.*, 1927, **130**, 2063.
[5] Allmand and Hunter, *Trans. Faraday Soc.*, 1928, **24**, 300.
[6] Lewis and Rupert, *J.A.C.S.*, 1911, **33**, 299.
[7] Muller, *Z. physik. Chem.*, 1902, **40**, 158.
[8] Carmody, *J.A.C.S.*, 1929, **51**, 2905.

**Sodium Chloride.**—The British Drug Houses A.R. product was used untreated except for drying.

**Solutions** were made up by weight in an atmosphere of nitrogen.

## Results.

The results are given in Table I. Concentrations are given in gms. per 1000 gms. of water for each component salt. The first of the two figures given for each mixture is the E.M.F. of the cell
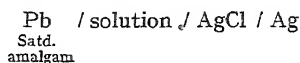
$$\text{Pb} \ / \text{solution} \ / \text{AgCl} \ / \text{Ag}$$
Satd.
amalgam

TABLE I.—E.M.F. IN VOLTS.

| NaCl gms. / PbCl gms.$^2$ | | 5. | 10. | 20. | 30. | 50. | 100. | 150. | 200. | 250. | 300. | Satd. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0·125 | $E$ | ·5369 | ·5275 | ·5215 | ·5190 | ·5187 | ·5215 | ·5279 | ·5339 | ·5408 | ·5473 | ·5557 |
|  | $a_1$ | ·0165 | ·0344 | ·0547 | ·0664 | ·0681 | ·0547 | ·0333 | ·0208 | ·0122 | ·00735 | ·00382 |
| 0·25 | $E$ | ·5272 | ·5184 | ·5127 | ·5102 | ·5092 | ·5128 | ·5185 | ·5250 | ·5315 | ·5388 | ·5469 |
|  | $a_1$ | ·0352 | ·0697 | ·1086 | ·1320 | ·1428 | ·1077 | ·0692 | ·0417 | ·0251 | ·0142 | ·00759 |
| 0·5 | $E$ | ·5174 | ·5092 | ·5033 | ·5010 | ·5002 | ·5038 | ·5094 | ·5159 | ·5222 | ·5290 | ·5376 |
|  | $a_1$ | ·0753 | ·1428 | ·2259 | ·2703 | ·2876 | ·2173 | ·1405 | ·0845 | ·0519 | ·0305 | ·0156 |
| 1·0 | $E$ | ·5078 | ·5001 | ·4943 | ·4921 | ·4914 | ·4945 | ·5007 | ·5065 | ·5125 | ·5195 | ·5280 |
|  | $a_1$ | ·1592 | ·2898 | ·4554 | ·5405 | ·5709 | ·4484 | ·2767 | ·1761 | ·1095 | ·0640 | ·0330 |
| 1·5 | $E$ | ·5021 | ·4949 | ·4890 | ·4869 | ·4861 | ·4896 | ·4957 | ·5017 | ·5079 | ·5141 | ·5224 |
|  | $a_1$ | ·2480 | ·4346 | ·6880 | ·8104 | ·8624 | ·6566 | ·4083 | ·2560 | ·1580 | ·0975 | ·0511 |
| 2·0 | $E$ | ·4984 | ·4909 | ·4853 | — | — | ·4858 | ·4919 | ·4981 | ·5040 | ·5104 | ·5185 |
|  | $a_1$ | ·3309 | ·5933 | ·9178 | — | — | ·8828 | ·5491 | ·3388 | ·2139 | ·1300 | ·0692 |
| 3·0 | $E$ | ·4921 | ·4858 | — | — | — | — | ·4869 | ·4925 | ·4989 | ·5051 | ·5133 |
|  | $a_1$ | ·5405 | ·8828 | — | — | — | — | ·8104 | ·5240 | ·3183 | ·1964 | ·1037 |
| 6·0 | $E$ | — | — | — | — | — | — | — | — | — | — | ·5046 |
|  | $a_1$ |  |  |  |  |  |  |  |  |  |  | ·2042 |
| 9·0 | $E$ | — | — | — | — | — | — | — | — | — | ·4915 | ·5003 |
|  | $a_1$ |  |  |  |  |  |  |  |  |  | ·5663 | ·2854 |
| satd. | $E$ | ·4842 | ·4842 | ·4842 | ·4842 | ·4842 | ·4842 | ·4842 | ·4842 | ·4842 | ·4842 | ·4842 |
|  | $a_1$ | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 |
| Grams PbCl₂ in satd. soln. | | 7·24 | 3·72 | 2·09 | 1·80 | 1·67 | 2·14 | 3·78 | 6·01 | 9·80 | 17·30 | 34·80 |

the values obtained with the chlorine electrode having been corrected by subtracting 1·0840 volts. It will be seen that all solutions saturated with lead chloride gave the value 0·4842 volts, since lead chloride is the solid phase in all such solutions, no complexes having been found by Deacon. This value differs from that found by Allmand and Burrage, *viz.*, 0·4837 volts, but agrees with that of Carmody.[8] The cell reaction for all mixtures is

$$\text{Pb} + 2\text{AgCl} \rightleftharpoons 2\text{Ag} + \text{PbCl}_2$$
(solid) (dissolved)
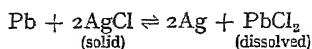
and variations in E correspond to variations in the activity of dissolved lead chloride. Following Allmand and Burrage, the activity of solid lead

chloride has been defined as unity, and this is also necessarily the value for dissolved lead chloride in the saturated solutions. Then if $a_1$ is the lead chloride activity in a mixture which gives an E.M.F. $E_1$, while $E_0$ is the E.M.F. of the cell containing a saturated solution,

$$E_0 - E_1 = 0.02957 \log a_1,$$

whence

$$\log a_1 = \frac{0.4842 - E_1}{0.02957}.$$

The second figure given in Table I. for each mixture is the activity calculated from this formula.

### Treatment of Results.

The equilibria in the condensed system NaCl—PbCl₂—H₂O, as determined by Deacon, give simpler curves than those found by Burrage for the corresponding potassium chloride system. Along the line AB
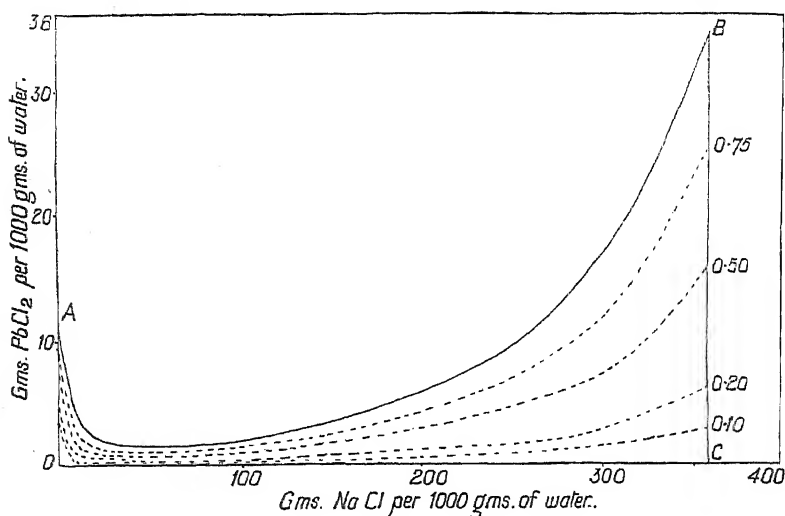


FIG. 1.

(Fig. 1) lead chloride is the solid phase, and along BC sodium chloride is the solid phase. Hence, on the convention adopted $a_1$ is unity along AB. Curves were drawn from the data as follows :—

   (1) $E$ against grams of NaCl at constant PbCl₂ concentration.
   (2) $E$ against grams of PbCl₂ at constant NaCl concentration.
   (3) $E$ against logarithm of PbCl₂ concentration, at constant NaCl concentration.

From these curves were read off PbCl₂ and NaCl concentration figures corresponding to definite values of $E$, which correspond to certain fractional values of $a_1$. The $E$ and $a_1$ values used are given in Table II. By means of the pairs of figures thus obtained, the broken curves of Fig. 1 have been drawn. They represent "isodynes" (Allmand and Burrage) or lines of constant activity of a component, in this case lead chloride. The terminal points for these curves on the OA axis, which represent solutions of lead chloride alone in water, have been calculated from the data of Carmody. The terminal points along BC, where sodium chloride is

the solid phase, give the concentrations of lead chloride which give the activities shown, in saturated sodium chloride solutions.

By means of the Gibbs-Duhem equation, the activity of the third component, water, along BC can be found. If $N_1$, $N_2$, $N_3$ and $a_1$, $a_2$, $a_3$ refer to lead chloride, sodium chloride and water respectively,

$$N_1 \, d \ln a_1 + N_2 \, d \ln a_2 + N_3 \, d \ln a_3 = 0.$$

Since along BC

$$a_2 = 1,$$

then

$$d \ln a_3 = -\frac{N_1}{N_3} \, d \ln a_1$$

TABLE II.

| E. | $a_1$. |
|---|---|
| 0·4880 | 0·75 |
| 0·4931 | 0·50 |
| 0·5049 | 0·20 |
| 0·5138 | 0·10 |

from which $a_3$ can be found by graphical integration, using the $a_1$ values along BC. The data for this calculation are given in Table III. The first column gives the lead chloride activity, the second and third its concentration in grams and mols, and the fourth the mol ratio of lead chloride to water. This fraction was graphed against log $a_1$ and from the area under the curve the $a_3$ values in the fifth column were found, assuming the activity of water in saturated sodium chloride solution as 0·7525. This was obtained from the data of Leopold and Johnston,[9] interpolation from their figures at various temperatures giving 17·88 mm. Hg as the vapour pressure of water over saturated sodium chloride solution at 25° C. It will be seen that the addition of 34·8 gms. of lead chloride, or 0·125 mols, to give saturation with respect to this salt, lowers the activity of the water from 0·7525 to 0·7509.

TABLE III.

| $a_1$. | PbCl$_2$. | | $N_1/N_3$. | $a_3$. |
|---|---|---|---|---|
| | gms. | mols. | | |
| 0·01 | 0·32 | 0·00115 | 0·000021 | 0·7525 |
| ·02 | 0·62 | ·00223 | ·000040 | ·7525 |
| ·05 | 1·46 | ·00526 | ·000095 | ·7525 |
| ·1 | 2·88 | ·01037 | ·000187 | ·7524 |
| ·2 | 6·10 | ·02196 | ·000396 | ·7522 |
| ·5 | 16·22 | ·05834 | ·001051 | ·7518 |
| ·6 | 19·72 | ·07099 | ·001278 | ·7516 |
| ·7 | 23·58 | ·08489 | ·001530 | ·7515 |
| ·8 | 27·07 | ·09745 | ·001756 | ·7513 |
| ·9 | 30·73 | ·1106 | ·001992 | ·7511 |
| ·95 | 32·73 | ·1179 | ·002123 | ·7510 |
| 1·0 | 34·80 | ·1253 | ·002257 | ·7509 |

In the absence of information about the activity of either water or sodium chloride along AB, it is not possible to determine the sodium chloride isodynes. It is not proposed in this paper to discuss the activity of lead chloride in presence of sodium chloride calculated in the usual manner relative to infinite dilution as the standard state, as more extensive measurements on solutions dilute with respect to both salt components are being carried out.

[9] Leopold and Johnston, *J.A.C.S.*, 1927, 49, 1974.

## Summary.

1. Measurements have been made of the activity of lead chloride in presence of sodium chloride in aqueous solutions up to saturation with both salts.

2. " Isodynes " or lines of constant lead chloride activity have been constructed.

3. The effect of the addition of lead chloride on the activity of water in saturated sodium chloride solutions has been calculated.

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# A THERMODYNAMIC STUDY OF SYSTEMS OF THE TYPE PbCl₂—RCl—H₂O AT 25° C. PART IV.

By H. N. PARTON.

The 25° C. isothermal for the condensed system PbCl₂—LiCl—H₂O has been obtained by Deacon,[1] and his results are shown by the continuous curve of Fig. 1. This paper records the electrometric study of



Gms. Li Cl. per 1000 gms. of water.
Solid phases—Pb Cl₂ along AB and Li Cl, H₂O along BC.
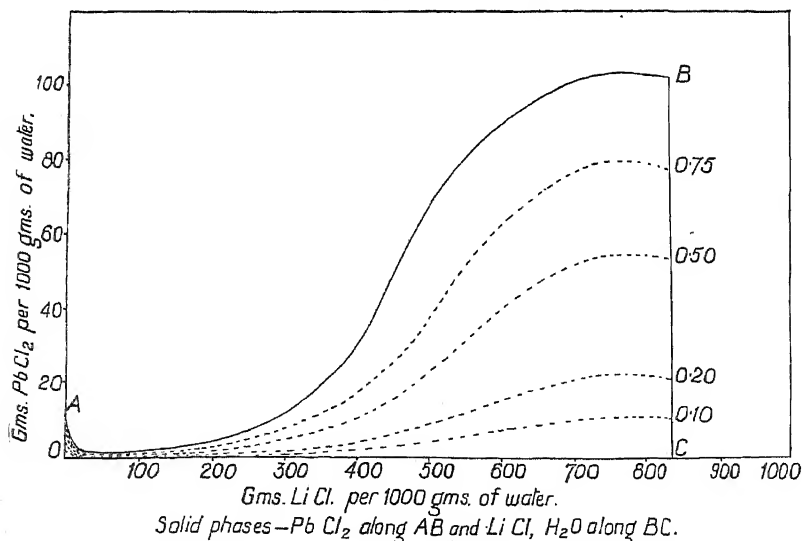
FIG. 1.

both saturated and unsaturated solutions in the same system, Parts I.[2] and II.[3] of the series having described the work of Allmand and Burrage

[1] Deacon, *J.C.S.*, 1927, **130**, 2063.
[2] Allmand and Burrage, *Trans. Faraday Soc.*, 1927, **23**, 470.
[3] *Ibid.*, 1933, **29**, 679.

on the system PbCl—KCl—H$_2$O, and Part III.[4] that of Miss Brasher and the present author on the system PbCl$_2$—NaCl—H$_2$O.

The experimental method was the same as that described in the preceding paper, silver chloride electrodes having been used for solutions containing up to 200 gms. LiCl per 1000 gms. of water, and the chlorine electrode for the more concentrated solutions. The solutions near satura-

TABLE I.

| PbCl$_2$ gms. \ LiCl gms | | 2. | 4. | 10. | 20. | 50. | 100. | 200. | 400. | 600. | 750. | Satd. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ·125 | E | ·5407 | ·5308 | ·5209 | ·5144 | ·5117 | ·5134 | ·5239 | ·5477 | ·5658 | ·5690 | ·5679 |
| | $a_1$ | ·0123 | ·0266 | ·0573 | ·0953 | ·1174 | ·1029 | ·0454 | ·0071 | ·0017 | ·0014 | ·0015 |
| ·25 | E | ·5315 | ·5218 | ·5122 | ·5057 | ·5032 | ·5056 | ·5163 | ·5398 | ·5575 | ·5599 | ·5594 |
| | $a_1$ | ·0251 | ·0535 | ·1129 | ·1875 | ·2277 | ·1889 | ·0820 | ·0132 | ·0033 | ·0028 | ·0029 |
| ·50 | E | ·5221 | ·5135 | ·5032 | ·4965 | ·4946 | ·4968 | ·5084 | ·5310 | ·5485 | ·5517 | ·5510 |
| | $a_1$ | ·0524 | ·1021 | ·2277 | ·3837 | ·4447 | ·3748 | ·1519 | ·0262 | ·0067 | ·0052 | ·0055 |
| 1·0 | E | ·5128 | ·5047 | ·4940 | ·4879 | ·4867 | ·4891 | ·5002 | ·5225 | ·5397 | ·5441 | ·5435 |
| | $a_1$ | ·1077 | ·2026 | ·4662 | ·7498 | ·8230 | ·6826 | ·2876 | ·0507 | ·0133 | ·0096 | ·0100 |
| 1·5 | E | ·5082 | ·5000 | ·4892 | — | — | ·4848 | ·4957 | ·5175 | ·5354 | ·5391 | ·5379 |
| | $a_1$ | ·1543 | ·2920 | ·6775 | — | — | ·9543 | ·4083 | ·0746 | ·0185 | ·0139 | ·0152 |
| 2·0 | E | ·5036 | ·4960 | — | — | — | — | ·4923 | — | — | — | — |
| | $a_1$ | ·2208 | ·3989 | — | — | — | — | ·5322 | — | — | — | — |
| 3·0 | E | ·4970 | ·4906 | — | — | — | — | ·4879 | ·5089 | — | — | — |
| | $a_1$ | ·3691 | ·6074 | — | — | — | — | ·7498 | ·1461 | — | — | — |
| 4·0 | E | ·4930 | — | — | — | — | — | — | — | — | — | — |
| | $a_1$ | ·5039 | — | — | — | — | — | — | — | — | — | — |
| 6·0 | E | ·4863 | — | — | — | — | — | — | — | — | — | — |
| | $a_1$ | ·8492 | — | — | — | — | — | — | — | — | — | — |
| 10·0 | E | — | — | — | — | — | — | — | ·4941 | ·5110 | ·5150 | ·5143 |
| | $a_1$ | — | — | — | — | — | — | — | ·4626 | ·1241 | ·0908 | ·0962 |
| 20·0 | E | — | — | — | — | — | — | — | ·4875 | ·5023 | ·5065 | ·5060 |
| | $a_1$ | — | — | — | — | — | — | — | ·7734 | ·2442 | ·1761 | ·1831 |
| 40·0 | E | — | — | — | — | — | — | — | — | ·4931 | ·4980 | ·4972 |
| | $a_1$ | — | — | — | — | — | — | — | — | ·5000 | ·3414 | ·3634 |
| 60·0 | E | — | — | — | — | — | — | — | — | ·4885 | ·4927 | ·4915 |
| | $a_1$ | — | — | — | — | — | — | — | — | ·7155 | ·5158 | ·5663 |
| satd. | E | ·4842 | ·4842 | ·4842 | ·4842 | ·4842 | ·4842 | ·4842 | ·4842 | ·4842 | ·4842 | ·4842 |
| | $a_1$ | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 |
| PbCl$_2$ in satd. soln. | | 7·15 | 4·40 | 2·20 | 1·69 | 1·44 | 1·80 | 4·55 | 30·4 | 91·0 | 103·6 | 101·6 |

tion with respect to lithium chloride were somewhat viscous, and the attainment of equilibrium with the chlorine electrode tended to be slow. Also the change of the potential of this electrode on varying the amount of chlorine in the nitrogen-chlorine mixtures used, was also slow. For this

[4] This vol., p. 681.

reason the accuracy of the measurements for cells containing these strong solutions was less than that for the more dilute solutions. This is unfortunate, as the saturated solutions are of particular interest, not only because they give the terminal points of the " isodynes " but also because of the maximum found in Deacon's solubility curve (see below).

## Results.

The results are recorded in Table I., the E.M.F. values and the activities being given as in the preceding paper. The variations in the activity of lead chloride in presence of increasing quantities of lithium chloride are similar to those found in the potassium and sodium chloride systems, except that at constant lead chloride concentration, curves of lead chloride activity against lithium chloride concentration all pass through minima at about 750 gms. of LiCl per 1000 gms. of water. Despite the experimental uncertainty of about $\pm 0.5$ mv., the E.M.F.s of the cells containing saturated solutions of lithium chloride were definitely a little lower than those of cells containing 750 gms. of LiCl per 1000 gms. of water. This might be expected from Deacon's work (Fig. 1, solid line) as at 750 gms. LiCl, a greater amount of lead chloride is needed to attain saturation, and hence unit activity, than for saturated LiCl solutions.

## Treatment of Results.

The observed E.M.F.s were plotted as in the previous communication against (1) log $[PbCl_2]$ in grams per 1000 gms.of water (2) the square root of the lithium chloride concentration (3) the lead chloride concentration, and from the sets of curves, the concentrations of the two salts which give definite fractional values for the lead chloride activity were read off. From these figures, the lead chloride " isodynes " for the system have been constructed and are shown in Fig. 1 as broken lines. The isodynes bear a similar relationship to the solubility curve, as has been found in the systems containing sodium and potassium chlorides. They all pass through a maximum at about 750 gms. of LiCl per 1000 gms. of water.

## Discussion.

The relative effects of the addition of the alkali halides to aqueous solutions of lead chloride on the activity of the latter will be discussed at a later date when the results of further measurements on dilute solutions become available. In general, it may be said, that at the same ionic strength, the activity coefficient of lead chloride is greatest in presence of lithium chloride, and least in presence of potassium chloride. With increasing concentration of added alkali halide, at constant lead chloride concentration, the activity coefficient of the latter is continuously decreased. These results point qualitatively to the formation of complex ions, potassium chloride being most effective and lithium chloride least effective in forcing the lead ions into the complex anion. This agrees with the solubility results of Deacon and Burrage, as the latter found that stable solid complexes could be produced in the system $KCl$—$PbCl_2$—$H_2O$, while the former found no solid complexes in the other two systems.

Deacon noted that the solubility of lead chloride passed through a maximum shortly before the eutectic point was reached at which the solid phases $PbCl_2$ and $LiCl . H_2O$ can co-exist. No similar effect was found in the other systems. Such a maximum must be the result of two

opposing effects. It may be suggested that the complex formation which is the probable cause of the increasing solubility of lead chloride with increase in lithium chloride concentration, is opposed by the co-ordination of water by lithium ions, removing some water molecules from their role of solvent, and thus causing the observed maximum. Such co-ordination might be expected to show an effect when lithium chloride is the added salt, as the lithium ion is known to be highly hydrated, the solubility of lithium chloride is very large, and the solid in equilibrium with the saturated solution is the hydrate $LiCl \cdot H_2O$. The E.M.F. figures showed that the activity of lead chloride passed through a minimum, in the case of the unsaturated solutions, and this is the result to be expected if some of the solvent is removed by co-ordination.

### Summary.

1. The activity of lead chloride in aqueous solution has been determined in presence of lithium chloride.

2. " Isodynes " or lines of constant activity of lead chloride have been constructed.

3. The effects of the addition of potassium, sodium and lithium chlorides on the activity of lead chloride have been briefly compared.

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# KINETICS OF RECOMBINATION OF BROMINE ATOMS.

By E. Rabinowitch and H. L. Lehmann.

## I. Introduction.

The kinetics of recombination of free atoms have been studied so far almost exclusively on active hydrogen. For the understanding of a great number of thermal and photochemical reactions, the mechanism of recombination of *halogen* atoms is of great interest. The velocity of recombination of bromine atoms has been calculated by Bodenstein and Luetkemeier[1] and by Jost and Jung[2] from the kinetics of the reaction $H_2 + Br_2 \rightarrow 2HBr$. This method involves definite assumptions about the complicated mechanism of this reaction. We have tried to measure the same velocity by a more direct physical method. Senftleben and Germer[3] have already shown that the physical properties —in their case the thermal conductivity—of strongly illuminated halogen vapours are appreciably changed by dissociation into atoms. Samson

[1] Bodenstein and Luetkemeier, *Z. physik. Chem.*, 1924, **114**, 208.
[2] Jost and Jung, *Z. physik. Chem.*, 1925, **B, 3**, 83; Jost, *ibid.*, 1929, 95.
[3] Senftleben and Germer, *Ann. Physik.*, 1929, [3], **2**, 847.

and Turner [4] were able to find the lines of atomic iodine in the absorption spectrum of illuminated iodine vapour.

In our experiments the dissociation of bromine molecules has been studied by measuring the decrease of the molecular absorption-coefficient of the illuminated vapour. From these measurements the equilibrium

$$Br_2 \rightleftharpoons Br + Br \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

in light is easily calculated, and since the velocity of decomposition is known from the number of quanta absorbed, the velocity of recombination can be calculated too.

The difficulties of this simple method are the smallness of the dissociation effect as obtained with any available light intensity, and the occurrence of certain disturbing thermal effects.

## II. Experimental.

A. **The optical arrangement,** based on the principle of compensation of two photoelectric currents, is shown in Fig. 1.

In all three stages the resistance of the bridge is the same—260 ohms —ensuring an unchanged sensitivity of the photocells; in both stages II. and III. the outer resistance of the galvanometer is 260 ohms, the lowest resistance giving an aperiodic deflection.

The two light beams coming from the lamp (9) and falling on the photocells (12) and (16) must be compensated very exactly—within 0·01 per cent.—in order that changes of absorption of the order of 0·01 to 0·1 per cent. produced by illuminating vessel (7) with the light from the arc (1), can be measured. The compensation is achieved by moving lens (13) along the rail and by turning the mirror (15).

Special precautions must be taken (a) to keep the voltage of the lamp (9) as constant as possible ; (b) to avoid all kinds of mechanical vibrations or changes of the optical system, as may be due to slow relaxation of tight screws ; to warming or cooling of lenses, etc.

The total intensity of each of the two beams gave rise to a photo-current of about $2 - 4 \times 10^{-6}$ amps.; a change of 0·01 per cent. of this intensity produced an additional current of $2 - 4 \times 10^{-10}$ amps., or a deflection of 1 to 2 mm. in stage III.

Unfortunately, in this last stage of compensation the galvanometer showed quick irregular vibrations with an amplitude of 2 to 3 mm., corresponding to about 0·02 per cent. of the total intensity of the beam. To eliminate them we have been obliged to take means from 30 or 40 single readings. We are not able to say what the cause of these residual vibrations is ; the insufficient constancy of the voltage applied to the lamp (9) remains the most likely point. The current for the lamp (9) was supplied by a 220 volt storage-battery and the voltage stabilised by three large 2 volt-accumulators connected in parallel with the lamp.

A system of screens has been used around vessel (7) to prevent scattered light from the arc reaching the photocells during illumination. The filter (11), transparent only below 5000 Å., makes the suppression of scattered light relatively easy.

### B. Determination of the Number of Quanta Absorbed.

The vessel (7) is illuminated uniformly by the arc, and the intensity of illumination is measured by the combination thermopile (8)-galvanometer, calibrated with a standard lamp from the U.S.A. Bureau of Standards. When light filtered

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[4] L. A. Turner and Samson, *Physic. Rev.*, 1928, **31**, 983 ; 1931, **37**, 1023, 1684.

with $CuSO_4$ is used and the bromine pressure in the vessel is $p = 5$ mm., the absorption is found to be 3·1 per cent. per cm. A correction factor 1·27 accounts for the reflections on the back wall of the vessel, and the glass window of the thermopile. Thus, to an energy flow $I$ * (per 9 cm. per sec.) recorded by the thermopile, there corresponds an energy-*absorption* :

$$I*_{abs} = 3·1 \times 10^{-2} \times 1·27 I* = 3·94 \times 10^{-2} I* \qquad . \quad (2)$$

in 1 c.c. of the gas. With a mean wave-length $\lambda = 4300$ Å (computed by superposition of the energy-distribution-curve of the arc, and the absorption-curves of $CuSO_4$ and of $Br_2$), this means an absorption of

$$N_{h\nu} = 8·62 \times 10^{16} \times I* \text{ quanta} \qquad . \qquad . \quad (3$$

per sec. in 1 c.c.
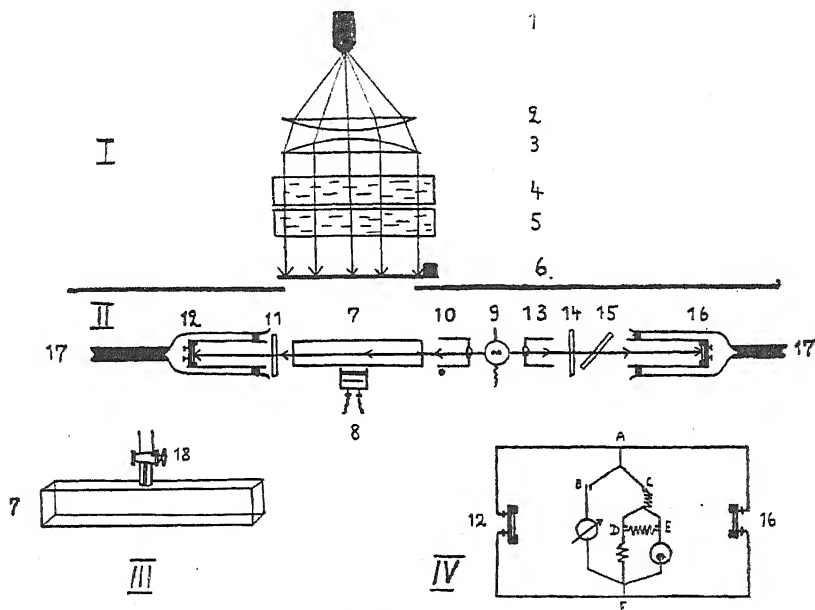
FIG. 1.

*I. Illumination.* 1. Self-regulating carbon arc, 25 amps., 1500 Watts. 2, 3. Glass lenses, 120 mm. diam. 4. Water, 3 cm. 5. $CuSO_4$ saturated, 3 cm. 6. Shutter, closing a hole 20 × 120 mm. in black cardboard separating the optical bench (17) from the arc.

*II. Absorption.* 7. Absorption vessel, rectangular, 20 × 20 × 120 mm., of optically flat quartz. 8. Moll thermopile. 9. Small tungsten filament lamp (6 volt, 24 watts), straight coil 2 mm. long, 1 mm. in diam., projected end-on. 10, 13. Two telescope eye-pieces, diameter 10 mm. 11, 14. Light filters, usually of Schott BG12 glass. 15. Mirror of clear glass rotatable on a horizontal axis. 12, 16. Selenium-iron photocells [Sueddeutsche-Apparate-Fabrik, Augsburg], enclosed in Dewar flasks. 17. Optical bench, made from heavy iron rail, supported by two stone slabs and isolated from the floor by thick layers of newspaper.

*III. Absorption Vessel on a larger scale.* 18. Stopcock greased with graphite-phosphoric acid mixture.

*IV. Photo-electric Circuit.* 12, 16. Photocells (internal resistance $\sim 10^4$ ohms). BF. Micro-ammeter (260 ohms.). C, DE. 2 Resistances, 245 ohms each. DF. Resistance 15 ohms. EF. Zernicke Galvanometer [Zc], resistance 15 ohms, scale 3 meter away.

The connections used for compensation were :—

Stage I. Microammeter : ABF : 1·0 × 10$^{-6}$ amps./degree.
,, II. Galvanometer : ACDF : 4·0 × 10$^{-9}$ amps./mm.
,, III. Galvanometer : ACEF : 2·3 × 10$^{-10}$ amps/mm.

For the calibration, the pair galvanometer-thermopile was used without additional resistances.   In the actual measurements, the sensitivity was lowered by means of shunts, so that 1 mm. deflection corresponded to

$$I * = 0·85 \times 10^{-3} \text{ watts}$$

or, after (3) to an absorption of $N_{h\nu} = 7·33 \times 10^{13}$ quanta in 1 c.c.   A deflection L thus meant an absorption :

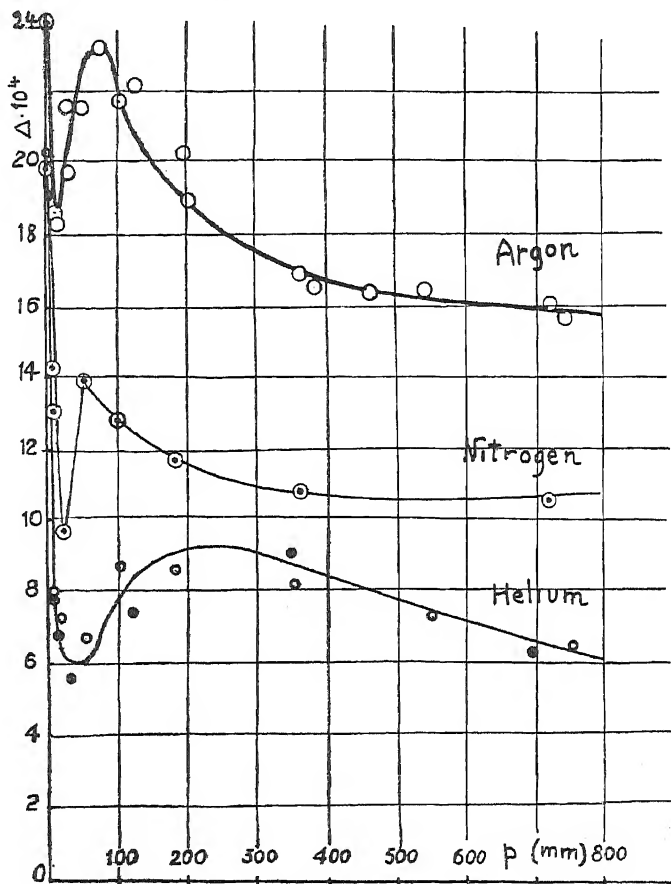$$N_{h\nu} = 7·33 \times 10^{13} \text{ L} \frac{\text{quanta}}{\text{c.c.} \times \text{sec.}} \qquad . \qquad . \qquad . \qquad (3a)$$



FIG. 2.

## C. A Typical Experiment was :

(a) To evacuate vessel (7) and measure the total intensity $I_0$ of the incident beam from lamp (9) by covering cell (16) and using the galvanometer in stage II.

(b) To let bromine enter vessel (7) from a container cooled down to — 33° C. (giving a pressure $p = 5$ mm. $Br_2$) ; to close the tap (18) and to measure the total absorption by bromine. With the light filter " Schott B.G. 12," the absorption was about 55 per cent.

(c) To uncover cell (16) and compensate the beams, first with the galvanometer in connection II., then in connection III.

(d) To illuminate vessel (7) with the arc and to note the deflections of the galvanometer $\Delta I$.   The shutter (6) is opened and closed for 30 or 40

times and readings taken 7 seconds after opening and after closing.    A mean value of $\Delta I$ is calculated.    Its reliability can be seen from the following example :

Single values of $\Delta I$ (in mm.), observed with 50 mm. Argon.

| Openings. | | | | | Mean | Closings. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 12 | 10 | 12 | 12 | 12 | | 11 | 13 | 13 | 10 | 14 |
| 10 | 8 | 12 | 5 | 14 | | 11 | 10 | 9 | 9 | 10 |
| 14 | 13 | 12 | 12 | 11 | | 13 | 10 | 12 | 15 | 10 |
| 10 | 11 | 10 | 10 | 12 | | 9 | 13 | 9 | 11 | 12 |
| 13 | 11 | 9 | 11 | 13 | | 10 | 11 | 10 | 11 | 11 |
| 11·8 | 10·6 | 11·0 | 10·0 | 12·4 | Mean | 10·8 | 11·4 | 10·6 | 11·2 | 12·4 |

11·2                    11·2                          11·1                    11·8

11·16                                        11·28

$11·2 \pm 0·1$
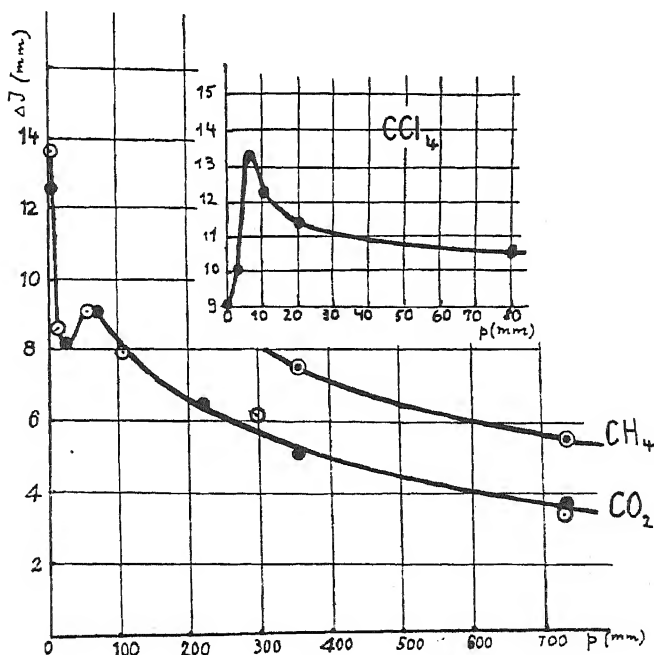


Fig. 3.

(e) To repeat the same experiment with increasing amounts of a foreign gas (He, A, $CO_2$, $N_2$, $CH_4$, $CCl_4$).    A curve showing the mean values of $\Delta I$ as a function of pressure is the result of such a set of measurements (Fig. 3).

## D. Calculation of the Change of Concentration.

From the change of absorption $\Delta I$ we must calculate the change of concentration $\Delta[Br_2]$.[5] The absorption being not small and the light non-monochromatic, a proportionality between $\Delta I$ and $\Delta[Br_2]$ cannot be expected. Fortunately, another simple relation holds for the concentrations used ; *the relative change of concentration is (almost exactly) proportional to the relative change of transmission* :

$$\Delta \equiv \Delta[Br_2]/[Br_2^\circ] \simeq - 2 \cdot 79 \, \Delta I/I_0 \qquad . \qquad . \qquad (4)$$

The symbol $\Delta$ will be used to denote the relative change of concentration, $\Delta[Br_2]/[Br_2^\circ]$, $[Br_2^\circ]$ being the original concentration of bromine. $I_0$ is the intensity of the incident beam.

Relation (4) is obtained as follows :
From the well-known formula

$$I = I_0 e^{-\alpha p_a a \ln 10} \qquad . \qquad . \qquad . \qquad . \qquad (5)$$

where $\alpha$ denotes the absorption coefficient, $p_a$ the pressure of $Br_2$ in atmospheres and $a$ the thickness of the vessel we get by differentiation :

$$d[Br_2]/[Br_2^\circ] = dp_a/p_a = - dI/I\alpha p_a a \ln 10 \qquad . \qquad . \qquad (6)$$

$\alpha$ and $I$ are *both* dependent on wave-length. Consider the product $\alpha I$ :

$$f = \alpha I = \alpha I_0 e^{-\alpha p_a a \ln 10} \qquad . \qquad . \qquad . \qquad (7)$$

This function has a maximum at $\alpha p_a a \ln 10 = 1$, that is to say at

$$I = I_0/e \simeq 0 \cdot 37 \, I_0 \qquad . \qquad . \qquad . \qquad (8)$$

or at 63 per cent. absorption. In the neighbourhood of this maximum $f$ changes very slowly with the wavelength. In the region 4000-5000 Å used by us, the absorption coefficients range from $\alpha = 3 \cdot 5$ to $\alpha = 7$, with $p_a = 0 \cdot 0065$ atm. and $a = 12$ cm., absorptions ranging from 50 to 70 per cent. In this whole region $f$ is nearly constant. For instance one calculates (see Table) :

| $\alpha$ | $\dfrac{I}{I_0}$ | $\dfrac{\alpha I}{I_0}$ |
|---|---|---|
| 7 | 0·285 | 2·00 |
| 5·6 | 0·366 | 2·05 |
| 4 | 0·487 | 1·95 |

The second row corresponds to the maximum of $\alpha I$. With the mean value $\alpha I = 2I_0$, (6) becomes :

$$d[Br_2]/[Br_2^\circ] = - dI/2p_a a \ln 10 I_0 = - 2 \cdot 79 \, dI/I_0 \qquad . \qquad . \qquad (9)$$

The changes of absorption and of concentration are in our experiments small enough to allow differences being put in the place of differentials ; thus (9) becomes equivalent to (4). The relation (4) is of general interest for measurements of concentration-changes by means of non-monochromatic light.

## E. Experimental Results.

The results with different gases are shown in Figs. 2 and 3, where the mean values of $\Delta I$ (Fig. 3) or of $\Delta = \Delta[Br_2]/[Br_2^\circ]$ (Fig. 2) are plotted against the pressure $p$ of the gases added.

As may be seen from the curves, $\Delta I$ (and $\Delta$) are rather complicated functions of $p$. Instead of a smooth decay-curve, which we first expected to obtain, we get curves showing first a minimum and then a maximum, finally approaching a constant value at high pressures rather than tending to zero. In the case of carbon tetrachloride the minimum is suppressed.

[5] Concentrations are given in number of *molecules* per c.c.

## III. General Discussion of the Curves.

The curves of Figs. 2 and 3 suggest a superposition of three elementary components. It is not difficult to find the effects involved. They are (A) thermal effect, $(B_1)$ dissociation limited by recombination on the walls, $(B_2)$ dissociation limited by homogeneous recombination.

### A. Thermal Effects.

Two such effects may be anticipated : changes of the concentration of bromine and changes of its absorption coefficient with temperature.

**(1) Concentration.**—The stop-cock (18) being closed during the measurements, the total amount of bromine in the vessel remains constant and the only concentration changes possible are those due to a difference of temperature between the axis of the vessel and the walls. The total heat absorbed during the measurement is too small to change appreciably the temperature of the walls, which can be assumed to be constant, $T_0$. The distribution can be easily calculated under the following simplifying conditions : first, an infinitely long cylindrical vessel, and second, no convection.

The equilibrium distribution of temperature in a cylindrical vessel with the radius $R$, in which $Q$ cal. of heat are absorbed every second in each c.c., is obtained by considering the energy flow through a cylindrical surface of unit length and putting this flow equal to the energy absorption inside :

$$2\pi r \kappa dT/dr = Q\pi r^2 \qquad . \qquad . \qquad . \qquad (10)$$

$dT/dr$ being the temperature gradient, $\kappa$ the heat conductivity and $r$ the radius of the surface. Integrating $dT$ from $r$ to $R$ we obtain the difference of temperatures between the point $r$ and the wall :

$$\Delta T_r = \int_r^R dT = Q(R^2 - r^2)/4\kappa \qquad . \qquad . \qquad (11)$$

With $Q = 1 \cdot 10^{-4}$ cal./sec., $R = 1$ cm. and $\kappa = 3 \cdot 10^{-5}$ one obtains for instance $\Delta T = 0 \cdot 8°$ C. for the temperature in the axis of the vessel $(r = 0)$.

The radial distribution of concentrations, $[X]_r$ (where $X$ denotes bromine or the gas added to bromine) is deduced from the condition that the pressure must remain uniform despite the differences of temperature :

$$[X]_r = Const/T_r = Const/(T_0 + \Delta T_r) \qquad . \qquad . \qquad (12)$$

The constant is determined by the total amount of gas in unit length of the vessel $\int [X]_r 2\pi r dr$ being equal to $\pi R^2 [X_0]$ where $[X_0]$ denotes the initial concentration. Taking $\Delta T_r$ from (11) we obtain :

$$Const = QR^2[X_0]/4\kappa ln(1 + QR^2/4\kappa T_0) \qquad . \qquad . \qquad (13)$$

By inserting (13) and (11) into (12) we get :

$$[X]_r = \frac{QR^2[X_0]}{4\kappa ln(1 + QR^2/4\kappa T_0)[T_0 + Q(R^2 - r^2)/4\kappa]} \qquad . \qquad (14)$$

with $QR^2/4\kappa T_0 \ll 1$ a development may be used for $ln(1 + QR^2/4kT_0)$ leading to

$$[X]_r = [X_0][1 + QR^2/8\kappa T_0 - Q(R^2 - r^2)/4\kappa T_0] \qquad . \qquad (15)$$

$$\Delta[X]_r/[X_0] = ([X]_r - [X_0])/[X_0] = QR^2/8\kappa T_0 - Q(R^2 - r^2)/4\kappa T_0 \qquad (16)$$

With $T_0 = 300°$, $R = 1$ cm., $\kappa = 3 \cdot 10^{-5}$ and $Q = 1 \cdot 10$ we get, for instance :

$$[X]_0 \simeq 0 \cdot 9986[X_0] \quad \text{and} \quad [X]_R = 1 \cdot 0014[X_0] \quad . \qquad . \qquad (17)\,(18)$$

for the concentrations in the axis of the vessel $(r = 0)$ and near the walls $(r = R)$.

It is interesting that the distribution of temperature and concentrations *does not depend on pressure.* This unexpected result is a consequence of the well-known fact that the viscosity and thermal conductivity of gases do not change with pressure.

The light beam passes through the vessel along the axis and has a diameter of 1 cm. The mean concentration of $Br_2$ in the path of the

beam is obtained by inserting into (17) the mean value of $(R^2 - r^2)$ between $r = 0$ and $r = 0.5$ cm., which is equal to $(R^2 - \frac{1}{8})$. This gives us

$$\overline{\Delta} = \overline{\Delta[Br_2]/[Br_2{}^\circ]} = -QR^2/8\kappa T_0 + Q/32\kappa T_0 \qquad . \quad (19)$$

or, with $R = 1$ cm.

$$\overline{\Delta} = -3Q/32\kappa T_0. \qquad . \qquad . \qquad . \qquad . \quad (20)$$

With the thermal effect alone (for instance with wave-lengths beyond 6100 Å.) the plot of $\Delta$ against $p$ would be of the type shown in Fig. 4. From a high value corresponding to the low heat conductivity of bromine, $\Delta$ would rapidly fall until the value corresponding to the higher conductivity of the gas added is attained, and then remain constant. The exact shape of the curve will depend on the heat conductivity of the gas mixture as a function of its composition.

(2) **Absorption-Coefficient.** The dependence of the absorption-coefficient of bromine on temperature has been measured by Ribaud ; [6] at $4 - 5000°$ Å. he found a decrease of 12 per cent. at 300 C. as compared with room temperature. Since the change of the absorption coefficient must be due to excitation of molecules to states of higher energy, its dependence on temperature must be of an exponential rather than a linear type. Thus the changes of $\alpha$ corresponding to temperature differences of 1 degree or less at room temperature—and such are the highest differences which may occur in our experiments according to (11)—must be less (probably much less) than $0.12/300$ or $0.04$ per cent. In the case of helium the changes must be even smaller than $0.004$ per cent.

## B. Dissociation.

The number of bromine atoms produced per second is :

$$d[Br]/dt = 2N_{h\nu}. \qquad . \qquad . \qquad . \qquad . \quad (21)$$

At low pressures, the velocity of recombination is determined by the time the atoms need for migrating to the walls ; at high pressures by the time necessary for homogeneous recombination.

**1. Diffusion Equilibrium.**—The problem of diffusion equilibrium is analogous to the problem of thermal equilibrium discussed above : $2N_{h\nu}$ atoms are produced per sec. per c.c. ; the velocity of their diffusion is determined by the coefficient $D$, and their concentration on the walls is always zero. Assuming an infinite cylindrical vessel with radius $R$, the law of the distribution of atoms is analogous to the law (11) :

$$[Br]_r = (R^2 - r^2)N_{h\nu}/2D = (R^2 - r^2)N_{h\nu}p/2D_0 \qquad . \quad (22)$$

$2N_{n\nu}$ taking the place of $Q$, and $D$ that of $\kappa$. The important difference is that $D$ is inversely proportional to the pressure.

The local change of concentration of $Br_2$ molecules in the case of diffusion equilibrium is not simply equal to (half) the local concentration of atoms, but is determined by two conditions :

    (a)   $[Br_2]_r + [Br]_r = const.$

    (b)   $\int_0^R ([Br_2]_r + \frac{1}{2}[Br]_r)2\pi r dr = \pi R^2[Br_2{}^\circ].$   .     .   (23)

[6] Ribaud, *Ann. Physique*, 1919, **12**, 107.

(a) is the condition of pressure being uniform throughout the vessel, (b) the condition of total amount of bromine being constant. By inserting (22) into (23) one calculates first the constant in (23):

$$const. = [Br_2^{\circ}] + N_{h\nu}\pi R^2/8D_0 \quad . \quad . \quad . \quad (24)$$

and then, from (23)(a) and (22):

$$[Br_2]_r = [Br_2^{\circ}] - N_{h\nu}p(3R^2/4 - r^2)/2D_0. \quad . \quad . \quad (25)$$

Integrating again from $r = 0$ to $r = 0.5$ we get, with $R = 1$ cm.

$$\overline{\Delta} = -5N_{h\nu}p/16D_0[Br_2^{\circ}] \quad . \quad . \quad . \quad (26)$$

as the mean change of concentration of $Br_2$ molecules in the path of light.

The dissociation effect as determined by diffusion equilibrium would thus be proportional to pressure, as schematically shown in Fig. 5.
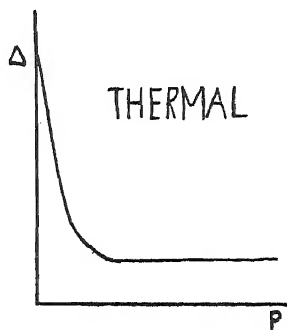


FIG. 4.
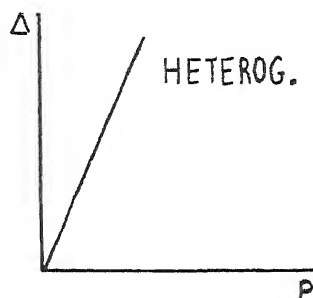
FIG. 5.
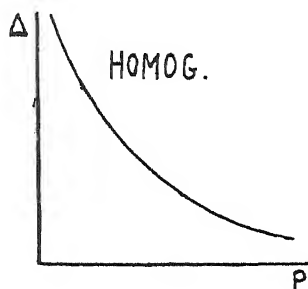


FIG. 6.
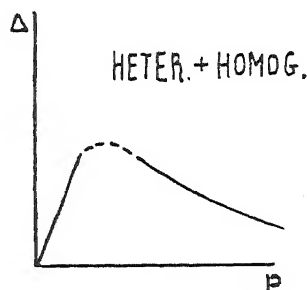
FIG. 7.

**2. Homogeneous Equilibrium.**—The generally accepted simple mechanism of recombination in " triple collisions "

$$Br + Br + X \rightarrow Br_2 + X \quad . \quad . \quad . \quad (27)$$
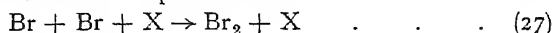
leads to the recombination velocity

$$- d[Br]/dt = C_1[Br]^2[X] \quad . \quad . \quad . \quad (28)$$

and together with (21) to

$$[Br] = \sqrt{2N_{h\nu}/[X]C_1} . \quad . \quad . \quad . \quad (29)$$

for the equilibrium concentration of the atoms, or to

$$\Delta = \tfrac{1}{2}[Br]/[Br_2^{\circ}] = \sqrt{N_{h\nu}/2[X]C_1}/[Br_2^{\circ}] \quad . \quad . \quad (30)$$

for the relative change of concentration of $Br_2$ molecules. (This simplified formula assumes that [X] is much greater than [Br_2], so that practically no recombination occurs with $Br_2$ as third body). The effect is inversely proportional to the square root of the pressure (Fig. 6).

**2a. The $Br_3$ Problem.**—In addition to this mechanism of recombination, the possibility of two others is suggested by the work of Rollefson and Eyring.[7] If the molecule $Br_3$ is really as stable as has been calculated by them, the recombination of Br- atoms may take place in one of the two following ways :

$$Br + Br_2 + X \rightarrow Br_3 + X \quad (C_2) \qquad . \qquad . \qquad . \quad (31a)$$
$$Br + Br_3 \rightarrow Br_2 + Br_2 \qquad . \qquad . \qquad . \quad (32a)$$
$$\text{or} \quad Br_3 + Br_3 \rightarrow Br_2 + Br_2 + Br_2 \quad (C_3) \qquad . \qquad . \quad (32b)$$
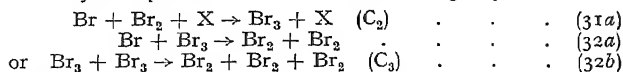
From the relatively high intensity of the effects observed by us we may conclude that either (31) or (32) must be a " slow " reaction. (The possibility of *both* having the same order of velocity may be disregarded as very improbable).

**Reaction (31) is Slow.**—In this case the bromine atoms will pass the greater part of their life as free atoms and only form $Br_3$ for a short time before recombination. The concentration of $Br_3$ would be small in comparison with that of Br and (32b) would disappear in comparison with (32a).

The velocity of recombination would be practically identical with the velocity of formation of $Br_3$ after (31a) :

$$- d[Br]/dt = C_2 [Br] [Br_2] [X] \qquad . \qquad . \qquad . \quad (33)$$

and the equilibrium concentration would be :

$$[Br] = 2N_{h\nu}/C_2 [Br_2] [X] \qquad . \qquad . \qquad . \quad (34)$$
$$\Delta = - N_{h\nu}/[Br_2^\circ]^2 C_2 [X] \qquad . \qquad . \qquad . \quad (35)$$

**Reaction (32) is Slow.**—Every bromine atom formed will practically at once find a partner to form $Br_3$. The concentration of Br would disappear in comparison with that of $Br_3$ and (32a) in comparison with (32b) ; velocity of formation of $Br_3$ will be given by (21). At equilibrium the change of concentration of $Br_2$ will be :

$$\Delta = - \tfrac{3}{2}[Br_3]/[Br_2^\circ] = - 3\sqrt{2N_{h\nu}}/2[Br_2^\circ]\sqrt{C_3} \qquad . \qquad . \quad (36)$$

In this case the relation (4) between $\Delta$ and $\Delta I$ would only hold if $Br_3$ has no absorption at all in the region 4000-5000 Å., which is hardly to be expected. If this is not so, the proportionality factor in (4) becomes an unknown quantity.

The three alternative laws (30), (35) and (36) lead to different predictions concerning the dependence of the dissociation effect on pressure, light intensity and concentration of bromine. They can thus be tested by comparison with experimental data.

## C. Superposition of the Three Effects.

(a) The heterogeneous recombination, giving a concentration of atoms which rises with increasing pressure, must correspond to the increasing part of the curves in Figs. 2 and 3 ; the homogeneous recombination corresponds to the declining part. In the region around the maximum the heterogeneous and homogeneous reaction occurs simultaneously, the mean " diffusion-time " being about equal to the mean " recombination-time." It is not difficult to state the conditions of equilibrium for this case too ; but since the velocity of the homogeneous reaction is now not uniform throughout the vessel its contribution must be calculated by integration, and we thus obtain an integral equation that must be solved. This can be done only by approximations, and a discussion of this equation would be premature in view of the inexactness of experimental data.

(b) The thermal effect would simply add to the dissociation effect —as small effects generally do—were it not for the fact that the amount of heat evolved in the gas increases considerably when the recombination becomes homogeneous. The recombination energy, absorbed by the walls in the heterogeneous region now remains in the gas.' In the heterogeneous region only excess energy (difference between the energy-quantum of the light and the dissociation energy of $Br_2$) is lost in the gas. Since the mean wave-length absorbed is 4300 Å., and the wave-length corresponding to dissociation limit is 6200 Å., the amount of heat absorbed in 1 c.c. at low pressures must be :

$$Q' = Q(6200 - 4300)/6200 = 0\cdot31Q \qquad . \qquad . \quad (37)$$

[7] Rollefson and Eyring, *J. Amer. Chem. Soc.*, 1932, **54,** 170.

where $Q$ denotes the *total* heat equivalent of the light absorbed :

$$Q = (N_{h\nu} \times 23 \cdot 0 \times 10^3 \times 10^8)/(6 \times 10^{23} \times 8110 \times 4300) \quad (38)$$
$$= 1 \cdot 10 \times 10^{-19} N_{h\nu};$$
$$Q' = 0 \cdot 34 \times 10^{-19} N_{h\nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38a)$$

In the heterogeneous region the thermal effect must correspond to the absorption of the heat $(38a)$, in the homogeneous region—to $(38)$. In the transitional region—dotted curve in Fig. 7, corresponding to the dotted region in Fig. 8—the thermal effect must increase to a value about three times larger than it was before.

As an ultimate result of this discussion, the experimental curves of Figs. 2 and 3 are to be interpreted as superpositions of a curve of type Fig. 8 (thermal effect) and a curve of type Fig. 7 (dissociation effect).
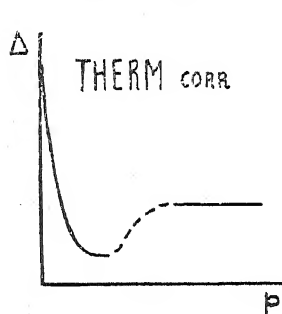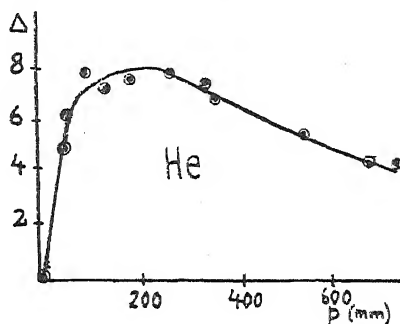


FIG. 8.                                   FIG. 9.

## IV. Quantitative Discussion.

### A. Estimation of the Thermal Effect.

Table II. contains the thermal effects as calculated after (20), (38) and $(38a)$.

TABLE II.—THERMAL EFFECTS.

|  | He. | A. | N₂. | CO₂. | CCl₄. | Br₂. |
|---|---|---|---|---|---|---|
| $\kappa \cdot 10^5 (21^\circ C.)$ | 35·4 | 4·15 | 6·14 | 3·5 | 1·4 | 1·05 |
| $\Delta$ { (low $p$) . | 0·30 | 2·53 | 7·73 | 3·0 | 7·5 | $10·3 \times 10^{-19} \times N_{h\nu}$ |
| { (high $p$) . | 0·97 | 8·29 | 5·60 | 9·7 | 25·0 | $33·7 \times 10^{-19} \times N_{h\nu}$ |

The thermal conductivity $\kappa$ of bromine, not yet measured, has been computed from its viscosity $\eta$ by means of the relation $\kappa = 1 \cdot 9\eta c_v$ known to be valid for other diatomic gases. With $\eta$ $(98 \cdot 1^\circ$ C.$) = 1 \cdot 81 \times 10^{-4}$ (*Rankine*) and the Sutherland-constant $C = 521 = (0 \cdot 88$ $T_k)$ we obtain $\eta$ $(27^\circ$ C.$) = 1 \cdot 48 \times 10^{-4}$, and with $c_v = 0 \cdot 0375$ cal/g, $\kappa$ $(27^\circ$ C.$) = 1 \cdot 05 \times 10^{-5}$.

The value of $N_{h\nu}$ in our experiments was $\sim 2 \times 10^{15}$. Comparison of Table II. with Figs. 2 and 3 shows that under these circumstances practically the whole of the effect observed in pure $Br_2$ and the predominant part of the effects observed in mixtures with A, $N_2$, and all other gases, *excepting* He, must be of thermal origin. Table III. shows it for the case of *pure bromine*.

TABLE III.—EFFECT IN PURE BROMINE.

| Experiments No. | | 1. | 2. | 3. | 4. | 5. | 6. |
|---|---|---|---|---|---|---|---|
| $10^4 \frac{[Br_4]}{[Br_2]}$ | observed | 19·2 | 20·4 | 29·0 | 20·5 | 24·4 | 27·5 |
| | thermal | 19·7 | 20·5 | 24·2 | 19·7 | 19·7 | 19·7 |
| | dissociation | | | | 1·2 | | |

Not only the order of magnitude, but also the absolute value of the calculated thermal effect is very close to the magnitude of the total effect observed. The dissociation, as computed according to (26) with the plausible value $D = 0·2$ for the diffusion of bromine atoms into bromine (see below), can be responsible only for a small fraction of the actual effect.

The sharp decrease of the effect observed on addition of small quantities of foreign gases—with the exception of $CCl_4$—must be due to the increase in the heat conductivity. From Table II. we expect this decrease to be most pronounced with helium, followed by other gases in the order nitrogen, argon, carbon-dioxide, carbon- tetrachloride. This expectation is fully justified by the curves in Figs. 2 and 3. The relations between the effects in pure bromine and bromine with 10 mm. of a foreign gas are

| X = | He. | $N_2$. | A. | $CO_2$ | $CCl_4$ |
|---|---|---|---|---|---|
| $\Delta(5 \text{ mm. } Br_2 + 10 \text{ mm. } X)/\Delta \text{ (pure } Br_2)$ | 0·36 | 0·57 | 0·65 | 0·68 | $> 1$ |
| $\kappa(Br_2)/\kappa(X)$ | 0·03 | 0·17 | 0·25 | 0·30 | 0·75 |

## B. The Dissociation Equilibrium in Helium.

In helium the thermal effect, even at the highest pressures, remains 2-3 times smaller than the dissociation effect. Under these circumstances the estimation of the thermal effect after (28) is exact enough to permit the dissociation effect being obtained by subtraction of the calculated thermal effect from the observed total effect. In Table IV. the actual data underlying the He-curve in Fig. 2 are treated in this way, the "low-pressure" value of Table II. being used for $p < 150$ mm., and the "high-pressure" value for $p > 150$ mm.

In Fig. 9 the pure dissociation effect in He, as calculated in Table IV. is plotted against pressure. The curve has the form of the "theoretical" curve in Fig. 7. The rising section, corresponding to the heterogeneous equilibrium, must obey equation (26) and can thus be used for the calculation of $D_0$, the *coefficient for the diffusion of Br-atoms into helium.* The three points belonging to this part of the curve give the values

$$D_0 = 0·31 \quad 0·41 \quad 0·51.$$

The mean value is $D_0 = 0·4$. The following are known diffusion coefficients for the diffusion of monatomic gases into helium :

| Ne into He. | A into He. | Kr into He (Extrapolated). |
|---|---|---|
| $D_0 = 0·93$ | 0·70 | 0·55 |

TABLE IV.—HELIUM.

$[Br_2^\circ] = 1.6 \times 10^{17}$    $I_0 = 1.50 \times 10^4$    $N_{h\nu} = 1.91 \times 10^{15}$.

| $p$(He). | $\Delta I$. | $10^4 . \Delta I/I_0$. | $\Delta$ Total. | $\Delta$ Thermal. | $\Delta$ Dissoc. | $10^{-13} \times \Delta[Br.]$ |
|---|---|---|---|---|---|---|
| 0 | 10·3 | 6·87 | 19·2 | 19·7 | ~ 0 | |
| 5 | 4·23 | 2·82 | 7·85 | | | |
| 11 | 3·70 | 2·47 | 6·80 | | | |
| 32 | 3·00 | 2·00 | 5·58 ⎫ | 0·57 | 5·01 | 8·0 |
| 120 | 3·98 | 2·65 | 7·40 ⎬ | | 6·83 | 10·9 |
| 350 | 5·00 | 3·33 | 9·30 ⎫ | 1·85 | 7·45 | 11·8 |
| 700 | 3·41 | 2·27 | 6·33 ⎭ | | 4·48 | 7·15 |

$[Br_2^\circ] = 1.6 \times 10^{17}$    $I_0 = 1.52 \times 10^4$    $N_{h\nu} = 1.99 \times 10^{15}$

| | | | | | | |
|---|---|---|---|---|---|---|
| 0 | 11·1 | 7·32 | 20·4 | 20·5 | ~ 0 | |
| 6 | 4·33 | 2·86 | 7·98 | | | |
| 14 | 4·00 | 2·64 | 7·35 ⎫ | | | |
| 50 | 3·70 | 2·44 | 6·80 ⎬ | 0·60 | 6·20 | 9·90 |
| 100 | 4·80 | 3·17 | 8·83 ⎭ | | 8·23 | 13·3 |
| 180 | 4·70 | 3·10 | 8·65 ⎫ | | 6·72 | 10·72 |
| 350 | 4·48 | 2·96 | 8·25 ⎬ | 1·93 | 6·32 | 9·93 |
| 550 | 4·05 | 2·67 | 7·42 ⎭ | | 5·49 | 8·77 |
| 760 | 3·60 | 2·37 | 6·60 ⎭ | | 4·67 | 7·49 |

The bromine atoms must be larger than the atoms of krypton, owing to the looser binding of the seven-electron-shell as compared with the closed eight-electron-shell of the krypton. The value 0·4 for the diffusion coefficient of bromine atoms into helium is therefore a very plausible one.

The values measured in helium beyond the maximum, corrected for the thermal effect, can be used for calculation of the velocity of homogeneous recombination. This is done in Table V.

TABLE V.—HOMOGENEOUS EQUILIBRIUM IN HELIUM.

| $p$. | $\Delta$ (Diss). | $\sqrt{p\Delta}$. | $p\Delta \times 10^{-1}$. | $C_1 . 10^{33}$. |
|---|---|---|---|---|
| 350 | 7·45 | 138 | 261 | 6·0 |
| 700 | 4·48 | 118 | 314 | 8·2 |
| 350 | 6·32 | 118 | 220 | 8·6 |
| 550 | 5·49 | 129 | 305 | 7·4 |
| 760 | 4·67 | 128 | 355 | 7·3 |
| $(a)$ | $(b)$ mean : | $(c)$ 126 | $(d)$ 291 | $(e)$ 7·5 |

The values of $\sqrt{p\Delta}$ show much better constancy than those of $p\Delta$. The mean deviation from the mean is 1·6 per cent. in column $(c)$ against 7 per cent. in column $(d)$, and there is no pronounced drift in $(c)$, whereas the values in $(d)$ increase with increasing pressure.

Table V. thus forms an argument for the simple mechanism $Br + Br + X \rightarrow Br_2 + X$ (" Br-mechanism ") and against the mechan-

isms involving $Br_3$. The $Br_3$-mechanism (31), (32$b$), leading to the law (36) with no dependence of the equilibrium on pressure at all, can be definitely excluded. The $Br_3$-mechanism (31), (32$a$), leading to the law (35), with the effect inversely proportional to the first power of pressure, must be considered at least as much less probable than the Br-mechanism (27), leading to (30) and to an inverse proportionality with the square root of the pressure.

Assuming the law (30) to hold, the velocity constant $C_1$ of the reaction $Br + Br + He \rightarrow Br_2 + He$ can be computed. The results are given in the last column of Table V. The mean value of $C_1$ is $7.5 \times 10^{-33}$ (with concentrations measured in number of molecules per .c.c.), corresponding to $2.7 \times 10^{15}$ if concentrations would be measured in mols per c.c. If we compute the number of " double collisions " between Br-atoms by means of the ordinary collision formula, using, with Steiner,[8] the value $\sigma = 4.5 \times 10^{-8}$ for the " collision-diameter " of a Br-atom, we find that our value of $C_1$ corresponds to 1 double collision $Br + Br$ in about 1300 being a " recombining " collision in helium at $p = 1$ atm.

## C. Dissociation Equilibrium in Other Gases.

The predominant rôle played by the thermal effect in all other gases used, makes the calculation of the dissociation-equilibria from the curves given in Figs. 2 and 3 too uncertain. So far only the following qualitative points can be stated :

The slope of the *rising* section, corresponding to the diffusion equilibrium must be a function of the molecular diameter $\sigma$. Since the position of the maximum is essentially determined by the steepness of the increasing section, these positions ought to go parallel with the molecular diameters. The following table confirms this :

| | He. | A. | $N_2$. | $CO_2$. | $CCl_4$. |
|---|---|---|---|---|---|
| Position of the maximum $p =$ | 200 | 75 | 60 | 60 | 10 mm. |
| Molecular diameter $\sigma = .$ | 1.9 | 2.9 | 3.0 | 3.1 | 6 Å |

The slope of the *declining* section of the curves must be characteristic of the homogeneous dissociation equilibrium. By differentiating (30) in respect to [X] we see that the higher the recombination constant, $C_1$, the flatter the curve. From Fig. 2 we may thus conclude that the constant $C_1$ is higher (about twice as high) for argon than for helium, and still higher for nitrogen. Fig. 3 indicates a lower value of $C_1$ for $CO_2$ and $CH_4$.

The value of the recombination constant obtained by us for helium ($2.5 \times 10^{15}$) may be compared with the value ($11.4 \times 10^{15}$) calculated by Jost[9] in the way mentioned for hydrogen as third body. The agreement of the orders of magnitude is already a very satisfactory result, if one bears in mind the differences in the methods used. That the value for $H_2$ would be higher than for He is to be expected, since

[8] W. Steiner, *Z. physik. Chem.*, 1932, (**B**) **15**, 249.
[9] *Cf.* reference 2. Jost's value $C = 5.7 \times 10^{15}$ is the constant of the equation $+ d[Br_2]/dt = C[Br]^2[X]$ and therefore half our $C_1$.

the number of collisions with $H_2$ must be higher owing to the greater molecular velocity (the molecular diameters of $H_2$ and He being nearly equal). The diatomic structure of $H_2$ may contribute in making the energy transfer easier.

There is one dubious point, discussed by Steiner ; when two bromine atoms meet, the statistical probability of their forming a $Br_2$ molecule in the ground state is only $1/30$ ; in 29 cases out of 30 some other term of the bromine molecule must be involved, giving a repulsion or only a weak attraction between the atoms. Will the " stabilisation " of the molecule by triple collision be only possible if the two atoms are on the " normal " attraction curve ? If so—and Steiner assumes it—our results would mean a very high probability of energy transfer. For instance, at atmospheric pressures, with He one collision in 45, with $H_2$ one in 10, with A or $N_2$ a still higher proportion of " favourable " double collisions would be " recombining " ones. This means either an extremely long life of the $Br_2$ " quasi-molecule," or an energy transfer over very great distances. There exists an alternative possibility : namely that the cases of " stabilisation " of $Br + Br$ are not confined to the occurrence of original attraction. Atoms meeting along a " repulsion curve " must have a certain probability of " jumping over " to the attraction curve in a " collisions of the second kind " if they are struck by a third body during their interaction. The probabilities of this process would be different for the different quantum states of the system ; but our whole experience concerning energy transfer during collisions allows us to expect that it cannot be generally neglected.

## D. Possible Errors.

The chief source of possible error of the results in the case of *helium* lies in the determination of the number of quanta $N_{h\nu}$ and arises from the non-uniform distribution of the light-intensity over the surface of the vessel, the uncertainty of the calculation of the " mean wave-length," and the absorption of a certain amount of light (not over 10 per cent. of the total) beyond the convergency limit, where it may produce dissociation with a probability less than 1 or even not produce it at all. The possible error of the determination of $N_{h\nu}$ we estimate to be about 15 per cent.

The thermal correction makes in the case of He 20 to 30 per cent. of the total effect observed. It may be slightly overestimated, due to the neglect of convection and to the assumption of an infinite vessel. The possible error introduced by this in the determination of $C_1$ may be of the order of 10 to 15 per cent. Thus, for the value of $C_1$ given above, we may claim an exactness of about $\pm$ 30 per cent. The results with other gases are preliminary ; we hope to be able to obtain better results by minimising the thermal correction. We will postpone until then the discussion of the relative efficiency of different gases in promoting the recombination and of the factors (molecular size, molecular velocity, mono- or polyatomic structure) determining this efficiency.

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## Summary.

1. By exact compensation of the photo-currents produced by two
light beams from the same light source in falling on two selenium-iron
photocells, intensity changes of 0·01 per cent. and less can be measured.

2. With this arrangement the stationary change of concentration of
molecules in bromine vapour illuminated with light from a high current
carbon arc can be detected.

3. This effect is due partly to dissociation of bromine into atoms
(dissociation effect), and partly to a non-uniform distribution of tempera-
ture and concentration in the illuminated vapour (thermal effect).

4. On addition of small quantities (5-10 mm.) of He, A, $N_2$, or other
gases to bromine (5 mm.) the effect *decreases* very considerably. This is
ascribed to the decrease of the thermal effect due to the higher thermal
conductivity of the gas added.

5. On addition of greater quantities of a foreign gas (order of 10-100
mm.) the effect *increases* again. This increase is due to the dissociation
effect becoming stronger with increase of the time the atoms need for
migrating to the walls (diffusion equilibrium).

6. If the pressure is raised still higher, the effect *reaches a maximum
and then decreases* slowly. This is due to the homogeneous recombination
of the atoms in the gas (homogeneous equilibrium).

7. At the highest pressures used, the effect tends to a constant value,
which is to be interpreted as the residual thermal effect.

8. Formulæ can be derived under certain simplified conditions for
the thermal, heterogeneous and homogeneous equilibria.

9. A comparison of these formulæ with the experimental curves shows
an agreement in the following points :

(*a*) The drop at low pressures is strongest with He, followed by $N_2$,
A, $CO_2$, and $CCl_4$, in accordance with the order of thermal conductivities.

(*b*) The increase at medium pressures is slowest, and the maximum is
situated at the highest pressure in He, followed by A, $N_2$, $CO_2$, $CCl_4$, in
accordance with the order of the *molecular diameters*. In the case of
helium the diffusion-coefficient of bromine atoms into helium can be
estimated from the experiments, and the plausible value $D = 0·4$ is
obtained.

(*c*) The decrease at *high pressures* is steepest with helium, followed
by argon and nitrogen. This means a higher efficiency of A and especi-
ally of $N_2$ in promoting homogeneous recombination of bromine atoms
as compared with helium.

10. Since the thermal effect means only a correction of about 20 per
cent. of the total in helium, the velocity of the homogeneous recombina-
tion of bromine in helium can be calculated with some accuracy. It
proves to be inversely proportional to the *square root* of pressure, in
accordance with the simple three-body mechanism :

$$Br + Br + X \rightarrow Br_2 + X$$
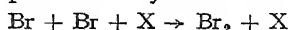
but not in accordance with possible mechanisms involving the molecule
$Br_3$.

11. The absolute value of the recombination constant of the reaction $Br + Br + He \rightarrow Br_2 + He$ is found to be $7\cdot5 \times 10^{-33}$ (concentrations in molecules per c.c.) or $2\cdot7 \times 10^{-15}$ (concentrations in mols per c.c.), meaning that about one double collision in 1300 is a "recombining" collision at atmospheric pressure. This number is rather high, being of the order of the total number of "triple collisions" to be expected from kinetic calculations.

It would be difficult to reconcile these high values with the theory of Steiner that only 1 out of 30 double collisions $Br + Br$ offers a possibility of stabilisation by a third body.

# REVIEWS OF BOOKS.

**Distortion of Metal Crystals.** By C. F. ELAM (Mrs. G. H. TIPPER). (Oxford, at the Clarendon Press. Pp. xlv + 186, with 94 diagrams and numerous plates. 1935. Price 15s. net.)

By a combination of circumstances the authoress of this important book has been led to describe her own pioneer work, as well as the investigations of a host of others, in a new volume of the Oxford Engineering Science Series. To cover the field of plastic deformation in metal crystals (including fracture) as Miss Elam has done is no light task; yet the reader is carried along with a strong sense of continuity, in spite of the wealth of detail and somewhat conflicting evidence which is characteristic of parts of the subject. The advent of this mine of information following closely upon the passing of Sir Alfred Ewing will not escape notice; it is a theme in which he always rejoiced, since the closing of last century when he and Rosenhain begun their labours at Cambridge and founded, in this country at least, the science of physical metallography.

Miss Elam rightly remarks that detailed knowledge of single crystals came long after we possessed a considerable amount of information about the physics of polycrystalline material : that we know what we do about single metallic crystals is very largely due to her classical experiments, both in their preparation and the study of the effects of strain.

Naturally, the basic questions of distortion and fracture, including the related matter of fatigue, are of major import for the engineer; there are certain aspects of these, however, which concern the physical chemist, and to them special attention may be directed. Chief, perhaps, is the distinction which we are more or less forced to draw between "ideal" and "real" crystals. The introduction of this touch of dualism into crystallography is largely the work of Smekal and his followers; in fact of all those who try to explain the age-long discrepancy between the calculated strength of materials and the values which appear in the laboratory. The answer is probably to be found, as Sir William Bragg has recently remarked, in the phrase "Unity is strength." Cracks, minute pores, and other imperfections regarded as deviations from the "ideal," are mainly responsible.

Alternative suggestions to account for the changes accompanying deformation are (1) Beilby's—that the material ceases to be crystalline and becomes amorphous, and (2) the view associated with the name of Tammann, Körber and others, that change of orientation is the cause.

All these theories have contributed, and no one of them appears to be lacking in consistency.

It remains to add an appreciation of the excellent format of the book, and of its moderate price. Its possession is something to be coveted by engineers and physical chemists alike.

F. I. G. R.

**Orthohydrogen, Parahydrogen, and Heavy Hydrogen.** By A. FARKAS· (The Cambridge Series of Physical Chemistry. Cambridge : The University Press, 1935. Pp. xiv + 215. Price 12/6 net.)

Although not " the first book on heavy hydrogen " as the notice on the dust-cover claims, this is the first in English, and it is more comprehensive than its French and German predecessors. The inclusion of ortho- and para-hydrogen is an excellent feature, since the book is now a monograph on the new forms of hydrogen. Although the mathematical theory is given in quite adequate detail, the book (like the others in the series which have so far been published) is also strong on the experimental side, the apparatus being well described and illustrated by clear and good diagrams. The experimental results are also fully summarised by means of tables and curves, and there is a bibliography of nearly three hundred references. Dr. Farkas is known for his own researches in this field, and his book may be expected to be authoritative. It is also very clearly written, and, apart from one or two obvious errors overlooked in proof-reading, is very well printed. The wider aspects of the subject, such as the use of the new forms of hydrogen in the solution of chemical and physico-chemical problems, are included, and altogether the book is one which can be warmly recommended to chemists. The only slight criticism which the reviewer has to offer is that too much of the text is in the footnotes, which are best reserved for literature references.

J. R. P.

# THE DIFFUSION OF NON-METALLIC ELEMENTS IN IRON AND STEEL.

By Arthur Bramley, Frederick Wardle Haywood, Arthur Thomas Cooper and John Thomas Watts.

## Introduction.*

Previous work by one of the authors and his collaborators [1] on the movement of carbon and nitrogen in iron and steel has shown that, when suitable precautions are taken to ensure uniformity of attack of the re-acting gases on the solid metal, these elements diffuse into or out of the steel in a perfectly regular manner, the movement following accurately Fick's law of diffusion. Quite a number of researches on this subject have been recorded by other investigators, but in nearly all cases in-sufficient attention to details has resulted in deductions being made which can only be regarded as approximate. In the papers referred to, full particulars are given of the necessary precautions that must be taken in order that the results obtained may be quantitative in character.

In the work about to be described, the rate of diffusion of sulphur, oxygen, and phosphorus has been investigated. Cylindrical bars of metal, similar in dimensions to those used in the previous work, were employed, and the method of heating and control of the attacking gases carefully attended to in order to secure uniformity of action over the whole area of the metal concerned.

The three elements mentioned above, when present in abnormally large concentrations in iron or steel, have a remarkable effect on the rate of diffusion of carbon in the metal. The magnitude of this effect has been investigated.

In Part IV. an account is given of the extraordinary way in which small quantities of oxygen present in the nitriding atmosphere, or as iron oxide dissolved in the iron, facilitate the nitriding of the metal and, in the latter case, increase the stability of the nitride formed.

## PART I.—THE DIFFUSION OF SULPHUR IN IRON AND STEEL.†

This subject does not appear to have attracted much attention in the past, the only reference of note being one due to Fry [2] who made a

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[1] Bramley and Jinkings, *Carnegie Scholarship Memoirs of the Iron and Steel Inst.*, 1926, **15**, 17-69 ; Bramley and Beeby, *ibid.*, 71-125 ; Bramley and Jinkings, *ibid.*, 127-153 ; Bramley, *ibid.*, 155-174 ; Bramley and Lawton, *ibid.*, 1927, **16**, 35-100 ; Bramley and Turner, *ibid.*, 1928, **17**, 23-66 ; Bramley and Haywood, *ibid.*, 1928, **17**, 67-87 ; Bramley and Lord, *ibid.*, 1929, **18**, 1-29 ; Bramley and Allen, *Engineering*, 22nd, 29th January, 19th February and 11th March, 1932.

[2] Fry, *Stahl und Eisen*, 1923, **43**, 1039.

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few measurements, but did not pursue the subject far.    This is somewhat surprising, in view of the possibility that knowledge of this kind might be of considerable importance in the metallurgy of iron and steel.

In Fry's experiments the cementing agent used was a solid powder made by heating iron and sulphur together.    In this the steel was embedded during the period of heating.    In the present investigation, it was considered desirable, for various reasons, to employ a gaseous cement if possible, and for this purpose a mixture of hydrogen and hydrogen sulphide was used.    This mixture was produced by passing hydrogen through boiling sulphur, and by adjusting the rate at which the hydrogen was passed through the sulphur, and subsequent addition of more hydrogen, a stream of gas of the required composition could be obtained for an indefinite period.
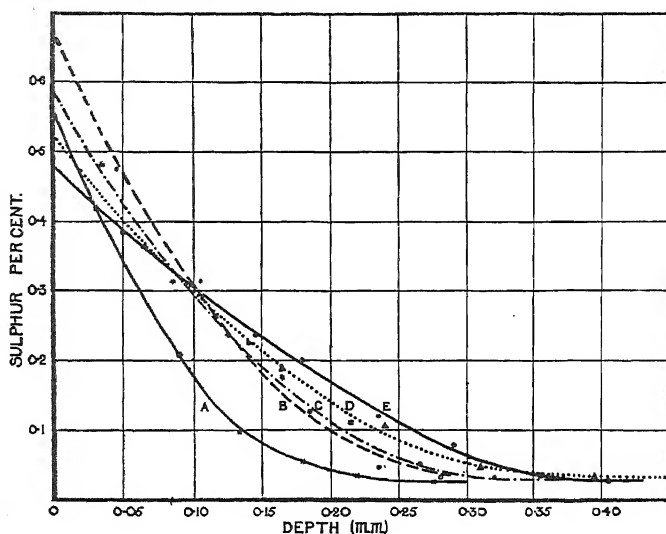


FIG. 1.—Sulphurisation of Swedish iron.

Curve A ——*——*—    40 hours at  950° C.   Experiment I.
  „    B —o—o—      „     „    1000° C.      „      II.
  „    C — · * — · *    „     „    1050° C.      „      III.
  „    D ···Δ···Δ··    „     „    1100° C.      „      IV.
  „    E —·—·—      „     „    1150° C.      „      V.

After many experiments, a process of heating the steel in a stream of gas containing 0·8 to 1·0 per cent. by volume of hydrogen sulphide, with intermittent periods of heating in hydrogen, was developed, which resulted in a perfectly uniform attack all over the surface, and at the same time the production of any appreciable amount of sulphide scale was avoided.    This was absolutely necessary, as it had previously been shown by Loebe and Becker [3] that there is a eutectic temperature at 985° C., the eutectic mixture containing slightly over 30 per cent. of sulphur.    It was therefore important to ensure that eutectic conditions were avoided, especially when higher temperatures were being used ; hence the method of intermittent periods of heating so that the metal could absorb all the sulphide produced.

[3] Loebe and Becker, *Z. anorg. Chem.*, 1912, **77**, 301.

Concentric layers of metal for analysis were obtained by turning in a precision lathe exactly as in the work previously mentioned. From the concentration of sulphur found in the metal at various depths below the surface the diffusion of this element under known conditions was determined. It was found that the diffusion of sulphur into iron is so slow that a treatment of at least 40 hours' duration was necessary to obtain a sufficient depth of penetration of the sulphur for a reasonable number of measurements to be made. This period of sulphurisation was adopted in all the experiments about to be described.

### TABLE I.

| No. of Expt. | Temp. $T$ abs. | Diffusivity Constant $K \times 10^{10}$. | $\log (K \times 10^{10})$. | $1/T \times 10^3$. |
|---|---|---|---|---|
| I | 1223 | 3·0 | 0·447 | 0·818 |
| II | 1273 | 5·5 | 0·740 | 0·785 |
| III | 1323 | 7·0 | 0·845 | 0·760 |
| IV | 1373 | 10·0 | 1·000 | 0·728 |
| V | 1423 | 13·0 | 1·114 | 0·703 |

### Series A.   Effect of Temperature.

The metal used was a very high quality Swedish charcoal iron containing 0·030 per cent. C, 0·080 per cent. Mn, 0·008 per cent. P, 0·010 per cent. S, and a trace of Si. Five experiments were made in which the sulphurisations were carried out at 950°, 1000°, 1050°, 1100°, and 1150° C. The analytical results are represented by the curves in Fig. 1. From the data obtained, the diffusivity constant $K$ for each temperature has been calculated by means of the formula previously used by Bramley and Jinkings.[1] The values of the constants obtained, in cm.[2] sec. units, are given in Table I.



Bramley and his co-workers have found that the diffusivity constant for carbon in iron and steel is connected with the temperature by a relationship of the form :

$$\log K = A/T + B,$$

in which $A$ and $B$ are constants. The graph shown in Fig. 2 drawn from the figures in the last two columns of the fore-

FIG. 2.—Relationship between the diffusivity constant $K$ and the temperature of sulphurisation.

going table, indicates that the relationship in the case of sulphur diffusion is slightly more complex than that indicated by the foregoing equation.

### Series B.   Sulphurisation of Carbon Steels.

In order to ascertain the effect of the presence of carbon on the rate of diffusion of sulphur in steel, experiments were made with three carbon steels having the compositions shown in Table II.

The process of sulphurisation applied to these three steels was exactly the same as that used on the Swedish iron in experiment II. The results obtained are shown graphically in Fig. 3, from which it is obvious that an

increase in the concentration of carbon has a very depressing effect on the rate of diffusion of sulphur in steel. The diffusivity constants were calculated where possible, and the relationship between these and the concentration of carbon in the steel are shown by curve A, Fig. 4. In the same figure, curve B shows the maximum depth of penetration of the sulphur.

It has been stated that Fick's law of linear diffusion is applicable to the movement of carbon in solid steel when there is a concentration gradient; the figures in Table III., showing the nature of the agreement between calculated and observed results for two cases selected from the experiments of this investigation, indicate that Fick's law is obeyed equally well by the diffusion of sulphur in iron and steel.

TABLE II.

|            | Expt. VI. | Expt. VII. | Expt. VIII. |
|------------|-----------|------------|-------------|
| Carbon .   | 0·125     | 0·410      | 0·965       |
| Silicon .  | 0·050     | 0·080      | 0·180       |
| Manganese .| 0·400     | 0·350      | 0·300       |
| Sulphur .  | 0·015     | 0·015      | 0·010       |
| Phosphorus .| 0·020    | 0·025      | 0·020       |

A similar agreement was obtained in all the other experiments.

Having found that the rate of diffusion of sulphur in steel is greatly retarded by the presence of carbon, an attempt was made to ascertain whether the diffusion of carbon was in any way affected by an increase in the concentration of sulphur in the metal. After a number of unsuccessful
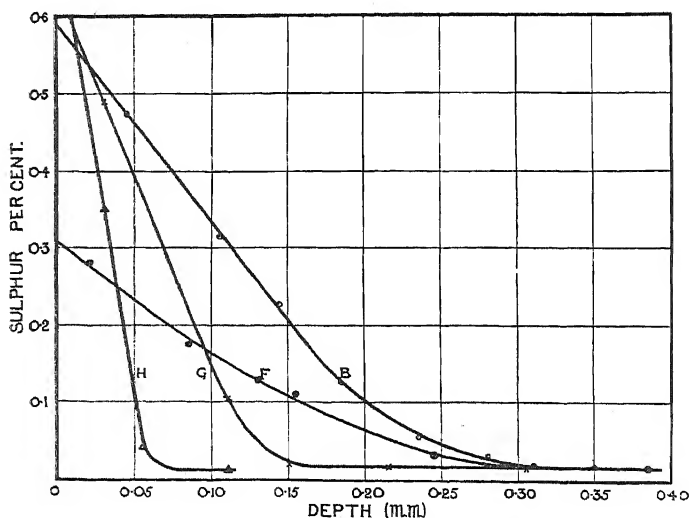


FIG. 3.—Sulphurisation of carbon steels.

| Experiment III. | Curve B. | Swedish iron. | | 40 hours at 1000° C. |
| ,, VI. | ,, F. | 0·125 per cent. C. steel. | ,, ,, ,, |
| ,, VII. | ,, G. | 0·410 ,, C. ,, | ,, ,, ,, |
| ,, VIII. | ,, H. | 0·965 ,, C. ,, | ,, ,, ,, |

efforts to obtain a bar of low carbon steel, high in sulphur but without the customary additional manganese, an attempt was made to carburise a bar of Swedish iron in an atmosphere of toluene vapour to which had been added about one-tenth of its weight of carbon bisulphide. The conditions of the experiment were such that, in the absence of the carbon bisulphide vapour, the concentration of carbon in the metal near the surface would

have been raised to well over 1 per cent.    Actually, the maximum concentration reached was little over 0·2 per cent.

Portions of bars of Swedish iron, previously sulphurised as in experiments III., IV., and V. were carburised by the method used by Bramley and Lawton.[1]    The results of these three experiments, numbers IX., X., and XI., in which the carburisations followed previous sulphurisations as per experiments III., IV., and V. respectively, are represented graphically in Figs. 5 and 6. Both carbon and sulphur were determined.    The curves S refer to the sulphur, the parts which rise continuously with



FIG. 4.—Effect of concentration of carbon on the diffusivity constant $K$, Curve A, and on the maximum depth of penetration of sulphur resulting from 40 hours' sulphurisation at 1000° C.

decrease in depth indicate the distribution of the sulphur before carburisation, whilst those passing through a maximum and falling with decrease in depth show the concentration of the sulphur after carburisation.

Apparently a little of the sulphur has been removed from the metal during the process of carburisation, probably by the action of hydrogen coming from the partial decomposition of the toluene vapour at the high temperature used.    The curve A in Fig. 6 shows the concentration of carbon at various depths resulting from a carburisation of the original Swedish iron for half the time, but otherwise under the same conditions as in the last three experiments.    The curves C in Figs. 5 and 6, which represent the distribution of the carbon, are remarkable in two ways.    They lie well below A, and are lower the higher the concentration of the sulphur in the surface layers of the metal before carburisation, thus showing that the presence of sulphur has a tremendous depressing effect on the rate of diffusion of carbon.    The other interesting feature is the very marked maxima and minima on these curves.    In all three cases the position of the maximum on the carbon curves coincides with the limit of penetration of the sulphur in the corresponding experiment.    For depths greater than those well beyond the limits of penetration of the sulphur, the carbon curves have the appearance of
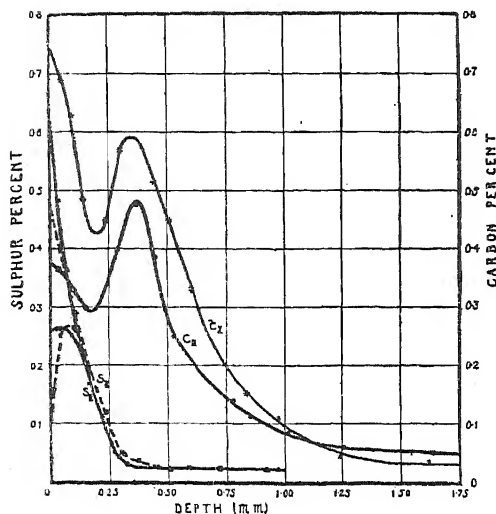
TABLE III.

**Experiment V.—Swedish Iron.**

Temp. of Sulphurisation 1150° C.

$K = 13·0 \times 10^{-10}$.

| Depth mm. | Sulphur Per Cent. | |
| --- | --- | --- |
| | Observed. | Calculated. |
| 0·05 | 0·380 | 0·380 |
| 0·10 | 0·290 | 0·290 |
| 0·15 | 0·225 | 0·220 |
| 0·20 | 0·165 | 0·160 |
| 0·25 | 0·110 | 0·110 |
| 0·30 | 0·075 | 0·080 |
| 0·35 | 0·050 | 0·055 |
| 0·40 | 0·035 | 0·040 |
| 0·45 | 0·025 | 0·030 |
| 0·50 | 0·025 | 0·025 |

**Experiment VI.—Steel.**

(0·125 Per Cent. Carbon.)

Temp. of Sulphurisation 1000° C.

$K = 3·5 \times 10^{-10}$.

| 0·05 | 0·245 | 0·245 |
| --- | --- | --- |
| 0·10 | 0·170 | 0·165 |
| 0·15 | 0·110 | 0·110 |
| 0·20 | 0·060 | 0·060 |
| 0·25 | 0·030 | 0·030 |
| 0·30 | 0·020 | 0·020 |
| 0·35 | 0·015 | 0·015 |

FIG. 5.

Experiment IX.   Curves $S_{IX}$ and $C_{IX}$.   Carbon
   and sulphur respectively in Swedish iron sul-
   phurised for 40 hours at 1050° C., and subse-
   quently carburised for 10 hours at 1000° C.
Experiment X.   Curves $S_X$ and $C_X$.   Carbon and
   sulphur respectively in Swedish iron sulphur-
   ised for 40 hours at 1100° C., and subse-
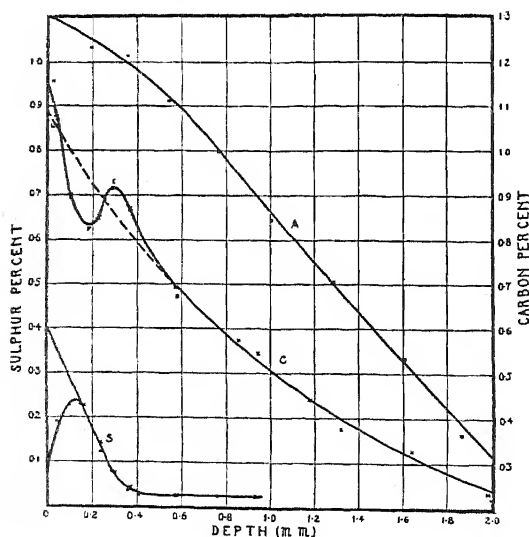   quently carburised for 10 hours at 1000° C.



FIG. 6.

Experiment XI.   Curves S and C.   Carbon and sulphur
   respectively in Swedish iron sulphurised for 40
   hours at 1150° C., and subsequently carburised for
   20 hours at 1000° C.
Curve A.   Carbon in Swedish iron after carburisation
   for 10 hours at 1000° C.

a normal diffusion curve. In Fig. 6 the curve C, of which the broken line part is an exterpolation of the lower portion, probably represents the actual distribution of the carbon at the termination of the period of carburisation, and immediately before the bar was allowed to cool down. This curve can be constructed by assuming a diffusivity constant of $7.5 \times 10^{-8}$. The actual distribution of the carbon, as found by analysis, has almost certainly resulted from a movement of the carbon from the position indicated by the broken line during the period of cooling. Such a redistribution of the carbon may be readily explained on the assumption that an increase in the concentration of sulphur causes a lowering in the solubility of the carbide in iron. The carbon has moved away from the region of high sulphur, increasing in concentration on both sides.

From the results of the foregoing experiments, it is concluded that :—

(*a*) The diffusion of sulphur in iron and steel proceeds in accordance with Fick's law, and that its rate of diffusion in iron, as measured by the diffusivity constants, is somewhat less than one three-hundredth of that of carbon and nitrogen at the same temperature.

(*b*) The rate of

diffusion of sulphur in steel is lowered by increasing the concentration of carbon, an increase of 0·5 per cent. of the latter element reducing the rate of diffusion of sulphur roughly 50 per cent.

(c) An increase in the concentration of sulphur in steel has a great depressing effect on the rate of diffusion of carbon in this metal.


PART II.—THE DIFFUSION OF OXYGEN IN IRON.*

When a carbon steel is heated in an atmosphere consisting of a mixture of carbon monoxide and carbon dioxide, carburisation or decarburisation may take place according to a number of conditions. The factors determining the particular reaction are :—

(a) the composition of the steel ;
(b) the temperature ;
(c) the composition of the gas mixture ;
(d) the gas pressure.

By a suitable combination of these factors it has been shown by Bramley and Lord [4] that the extent of decarburisation can be controlled. Further, by a suitable adjustment of the conditions, oxidation of the iron can be brought about simultaneously with the removal of carbon, and if the rate at which oxidation proceeds is so far restricted that the whole of the oxide formed remains dissolved in the metal, the surface of the latter should remain bright and show no signs of corrosion. This, of course, implies the existence of solid solutions of iron oxide in iron, and the consequent diffusion of the oxygen into the steel.

An attempt has been made to carry out experiments along these lines in the hope that a measure of the rate of diffusion of oxygen in iron might be obtained.

Preliminary experiments soon evinced the necessity of using high temperatures and extending the time of heating to very long periods. In the following experiment, No. XIII., a bar of Swedish iron was heated to 1100° C. for forty hours in a stream of gas consisting of 90 per cent. CO and 10 per cent. $CO_2$. After cooling the bar showed no signs of corrosion. Thin layers of the metal were turned off, and the oxygen estimated by Ledebur's method. The results are shown graphically by curve A, Fig. 7. Another experiment, No. XIV., was made in which the same metal was subjected to the action of a stream of gas consisting of 85 per cent. CO and 15 per cent. $CO_2$ for 100 hours at 1200° C. After allowing to cool, this bar was found to be covered all over with a very thin crystalline scale of iron oxide. This scale, which was too hard to turn off in the ordinary way, was removed by grinding with a fine emery wheel, the bar itself running between centres. This treatment left the metal with a mirror-like finish showing no signs of pitting. Samples for analysis were then removed by turning and the results obtained are shown by curve B, Fig. 7.

Two further experiments on the Swedish iron were made. In one of these, No. XV., a bar of the metal was heated to approximately 1000° C. for 100 hours in a furnace used for annealing white heart malleable iron castings ; in the other, No. XVI., a similar bar was heated for double this period.† Unfortunately, these two bars had suffered appreciable corrosion. However, the scale was ground off until the metal presented a bright surface,

* By Arthur Bramley and Frederick Wardle Haywood.
 † The authors are indebted to Messrs. Wm. Hammond & Co., Ltd., of Syston, Leicestershire, for passing these bars through one of their annealing furnaces.
 [4] Bramley and Lord, *J.C.S.*, 1932, 1641-1669.

after which thin layers were removed by turning and the analysis of these are shown by curves C and D in Fig. 7. The very steep parts of these two curves are almost certainly due to the presence of some free oxide in the turnings. Subsequent microscopic examination confirmed this, as distinct pitting of the metal and minute intrusions of iron oxide were found. Nevertheless, the form of these four curves left little doubt that definite diffusion of oxygen had taken place.

A microscopic examination of transverse sections of all the bars used in these experiments was made, the photomicrograph shown in Fig. 8 being prepared from the one used in experiment XIV. The etching agent used was an alcoholic solution of picric acid. There are one or two interesting features in the micrograph. Near the surface are a large number of spots which must be attributed to oxide, since their size and number fall off with increasing depth and the interior of the metal was found to be relatively free from them. It is interesting to note that there has been an appreciable segregation of this constituent in the major crystal boundaries, and that the limiting depth to which this segregation is visible was throughout the section approximately 1 mm. This, according to the analytical results, is the maximum depth of penetration of the oxygen in this experiment.



FIG. 7.

Experiment XIII. Curve A. Oxygen in Swedish iron after heating for 40 hours at 1100° C. in 90 per cent. CO and 10 per cent. $CO_2$ mix.

Experiment XIV. Curve B. Oxygen in Swedish iron after heating for 100 hours at 1200° C. in 85 per cent. CO and 15 per cent. $CO_2$ mix.

Experiment XV. Curve C. Oxygen in Swedish iron after heating for 100 hours at 1000° C. in annealing furnace.

Experiment XVI. Curve D. Oxygen in Swedish iron after heating for 200 hours at 1000° C. in annealing furnace.

The paucity of the data obtained in these four experiments, together with the uncertainty resulting from the intrusions already mentioned, makes it impossible to calculate the value of a diffusivity constant with any degree of accuracy, but the results would indicate that the value of this constant for a temperature of 1000° C. lies between $10^{-9}$ and $10^{-10}$.

With a view to obtaining further information on this subject, and at the same time avoiding the complications arising from oxide intrusions, a bar of Armco iron was deoxidised by heating in a slow stream of pure dry hydrogen for 100 hours at 1000° C. The effect of this treatment is shown graphically in Fig. 9, in which the circles indicate the results obtained by analysis. It was shown by Bramley and Allen [1] that the same values for

Depth (mm.)

0 —

0·5 —

1·0 —

FIG. 8.—Photomicrograph of Swedish iron after treatment as in experiment XIV. See curve B, Fig. 7. Magnification × 250.

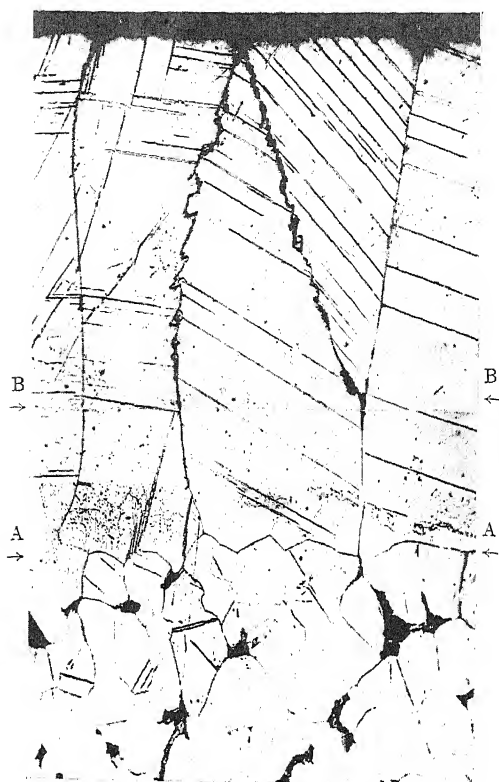FIG. 10.—Micrograph of section of bar used in experiment XVII. Magnification × 250.

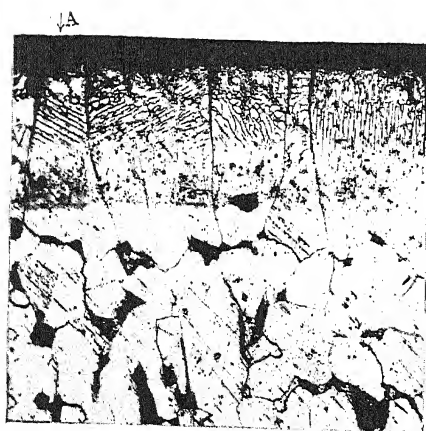FIG. 21.—Transverse section of bar used in Experiment VI.
Magnification × 200.

[See page 724.



FIG. 22.—0·15 per cent. carbon steel after phos-
phorising 40 hrs. at 1000° C.   Experiment
VII.   Magnification × 200.



FIG. 23.—Magnification × 150.

[See page 725.

the diffusivity constants for carbon in iron were obtained from decarburisation as from carburisation experiments, and it was anticipated that a similar method might be applied in the case of oxygen diffusion.  The relatively high concentration of oxygen in Armco iron made the latter a suitable metal for the purpose.  By the same method of calculation as that used by Bramley and Allen for carbon, the diffusivity constant for oxygen in iron was deduced from the results of the last experiment, No. XVII., and found to be $7 \cdot 5 \times 10^{-10}$ at $1000°$ C.  The crosses on the curve in Fig. 9 indicate the calculated figures. These show a perfect agreement with the experimental figures.

The photomicrograph shown in Fig. 10 was prepared from the bar of experiment XVII., and it bears out what has already been said regarding the previous micrograph.  The crystal boundaries down to a depth of $0 \cdot 3$ to $0 \cdot 4$ mm. are relatively fine.  Below this, they begin to thicken rapidly, large black spots appear, and these persist to the centre of the section.



FIG. 9.—Experiment XVII.—De-oxidation of armco iron.

According to Northcott[5] veining, or the existence of finer sub-boundaries within the larger crystal areas, results from the separation of dissolved oxide as the metal cools slowly.   The absence of veining from the surface to a depth of about $0 \cdot 3$ mm., then its progressive development as the depth increases to about $0 \cdot 6$ mm. when considered in conjunction with the curve shown in Fig. 9, is entirely in agreement with this view.

## Effect of Dissolved Oxide on the Carburisation of Iron.

A number of observations have been made[6] that the carburising property of any steel is impaired as a result of any treatment likely to cause oxidation.   The following experiments were made to study this effect in a more quantitative way than had been done hitherto.

Three pieces of Swedish charcoal iron were prepared from the same bar. Two of these were subjected to restricted oxidation, one for 100 hours at $1200°$ C. as per experiment XIV., and the other to 200 hours at $1000°$ C., as per experiment XVI.   After removing every sign of pitting by rubbing with fine emery cloth, the three bars were carburised under exactly the same conditions with the results shown in Fig. 11, in which A refers to the
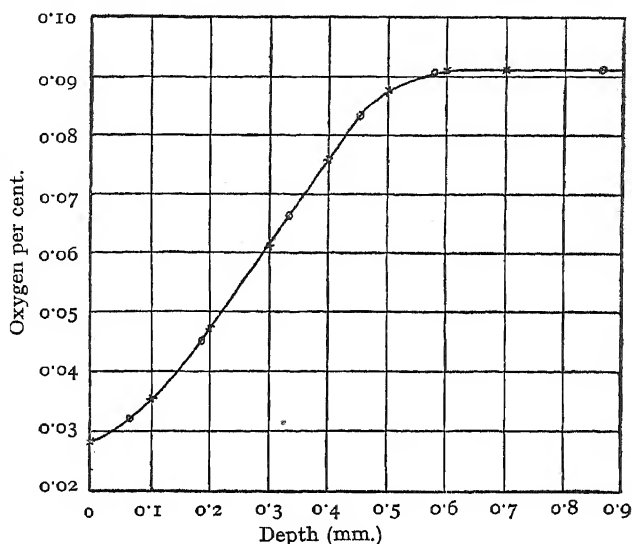
[5] Northcott, *J. Iron and Steel Inst.*, 1932, **126**, 267-287.
[6] Harder, Weber and Jerabek, *Trans. Amer. Soc. for Steel Treating*, 1928, **13**, 961.
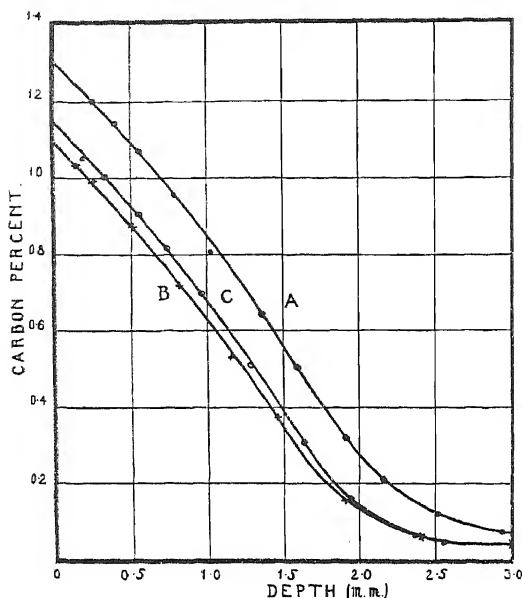
FIG. 11.—Swedish iron.

Curve A.   Carburised for 10 hours at 1000° C.
Curve B.   Oxidised as per experiment XIV. and subsequently carburised 10 hours at 1000° C.
Curve C.   Oxidised as per experiment XVI. and subsequently carburised 10 hours at 1000° C.
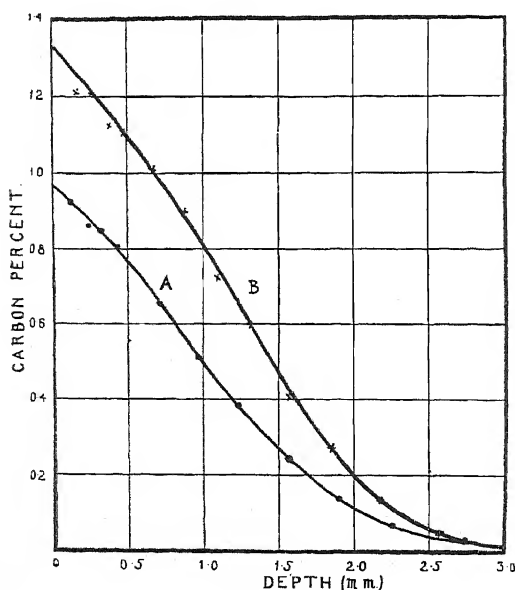


FIG. 12.

Curve A.   Armco iron after 10 hours' carburisation at 1000° C.
Curve B.   Armco iron, heated in pure dry hydrogen for 100 hours at 1000° C. and subsequently carburised for 10 hours at 1000° C.

bar used in the initial state, and B and C to the bars carburised after the treatment above-mentioned. Obviously, the oxidation has had an appreciable but not great detrimental effect on the carburising property of the metal. The diffusivity constants for carbon deduced from these three curves are $18 \times 10^{-8}$, $14 \times 10^{-8}$, and $15 \times 10^{8-}$ for A, B, and C respectively.

On the basis of the foregoing, it might be anticipated that the carburising properties of Armco iron might be improved by reduction of its oxygen content. This was verified in the following way :—

Two pieces of the metal were cut from the same bar, one was carburised in exactly the same way as in the three previous experiments, with the result indicated by curve A, Fig. 12, whilst the other was heated for 100 hours at 1000° C. in a steady stream of pure dry hydrogen before carburisation. The curve B, Fig. 12, shows the effect of this treatment. Obviously, the reduction of the oxygen in the Armco iron has enhanced its carburising properties very considerably. The diffusivity constant for carbon calculated from curve A for the original Armco iron is $12 \times 10^{-8}$, whilst that obtained for the reduced Armco iron corresponding to curve B, is $17 \times 10^{-8}$.

These experiments prove quite definitely that the presence of dissolved oxide has a detrimental effect on the carburising property of iron.

From this investigation it is concluded that :—

(a) Oxygen diffuses in iron ; the rate of diffusion, as measured by the diffusivity constant, being approximately a two-hundredth of that of carbon at the same temperature.

(b) The presence of dissolved iron oxide has a slight, but definite lowering effect on the rate of diffusion of carbon in the metal. This is very much less than that produced by sulphur.

## PART III.—THE DIFFUSION OF PHOSPHORUS IN IRON AND STEEL.*

In 1922 an investigation was carried out by Fry [7] into the diffusion of phosphorus and silicon in iron. The shape of the concentration depth curves he obtained indicated a relationship different from that required by the law of linear diffusion. In Fry's experiments, flat discs of iron were packed in a solid cementing agent rich in phosphorus, and after heating for a suitable length of time, layers for analysis were turned off the flat surfaces. His results appear somewhat erratic, and too few in number from which to draw definite conclusions. In the present investigation cylindrical bars were used, as this shape appeared to offer many advantages over that of the flat disc.

A gaseous cementing agent, consisting of a mixture of hydrogen and phosphine containing 10 per cent. of the latter, was used, but very great difficulty was experienced in obtaining uniform attack on the metal. Ultimately it was found that, by reducing the length of the bars to 10 cms. maintaining the diameter at 3·3 cms., and fixing them concentrically in a horizontal tube furnace so as to allow free passage of the gas around them, a perfectly uniform, thin scale of iron phosphide was produced on passing a very rapid stream of the gas through the furnace, reversing the direction of flow periodically and at the same time rotating the furnace itself. After an hour's treatment in this way, the bars were found to be covered with a thin, uniform and firmly adhering scale approximately 0·02 mm. thick, and containing a little over 20 per cent. of phosphorus. The furnace was then closed and the heating continued in an atmosphere of hydrogen. Samples for analysis were obtained as previously described, and the concentration of phosphorus estimated.

### Series C.

In the first series of experiments, Swedish charcoal iron was used, and the effect of varying the *duration of heating* was studied. In this series four experiments, Nos. I. to IV., were made in which the heating was maintained at 1000° C. for 7½, 20, 40 and 80 hours respectively, all other conditions being identical. The results of these experiments are shown graphically in Fig. 13, in which the full line curves A, B, C, and D refer to experiments I. to IV. respectively.

### Series D.

The **Effect of Temperature** on the rate of diffusion of phosphorus was next studied, but it was found that the variation of this factor could be

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* By Arthur Bramley and Arthur Thomas Cooper.
[7] Fry, Dissertation, *Die Diffusion der Begleitelemente des technischen Eisens in festes Eisen,* Berlin, 1922.

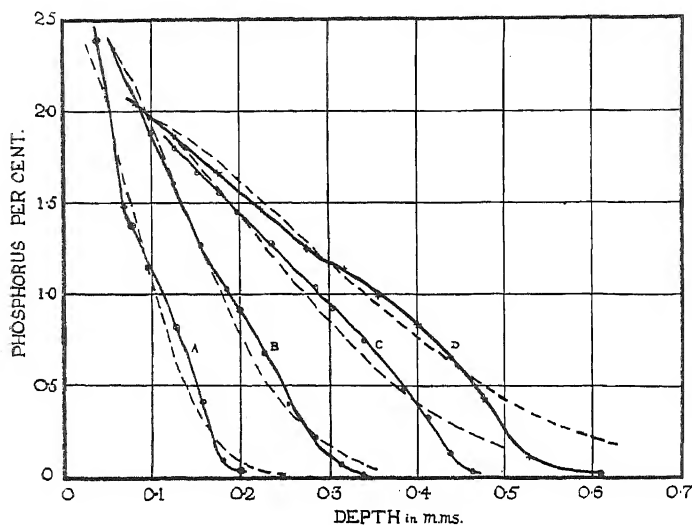investigated over a narrow range of temperature only, *viz.*, 950° C. to 1040° C. for the following reasons :—



FIG. 13.—Phosphorisation of Swedish iron.

Curve A.    Experiment I.    7½ hours at 100° C.
  ,,    B.        ,,        II. 20    ,,        ,,
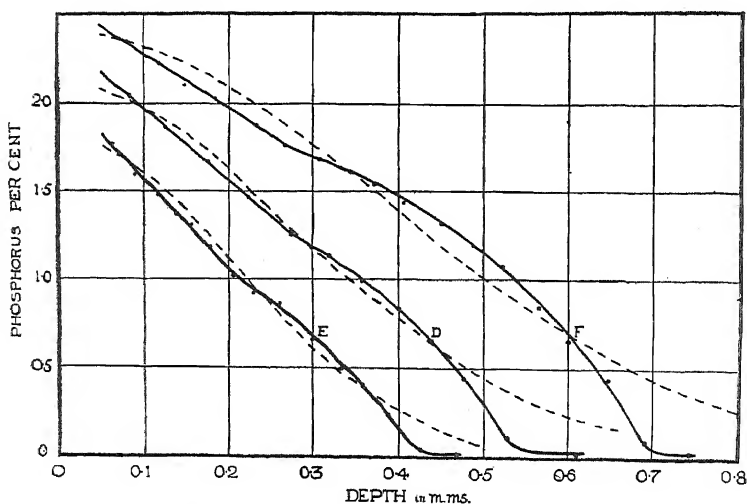  ,,    C.        ,,        III. 40    ,,        ,,
  ,,    D.        ,,        IV. 80    ,,        ,,



FIG. 14.—Phosphorisation of Swedish iron.

Curve E.    Experiment V.    80 hours at 950° C.
  ,,    D.        ,,        VI.  80 hours at 1000° C.
  ,,    F.        ,,        VII. 80 hours at 1040° C.

(1) Below 950° the rate of diffusion is so slow that a sufficient depth of metal is not affected in a reasonable length of time ; and (2) At a temperature of about 1050° C. fusion of the phosphide scale takes place, and it is necessary to avoid this.

Three experiments only, Nos. V., VI., and VII., were used for this purpose.   In each case the duration of heating was 80 hours.   The results are shown by the full line curves E, D, and F respectively, in Fig. 14.

The full line curves in Figs. 13 and 14 are obviously different from the concentration/depth curves obtained previously for the diffusion of carbon, nitrogen, sulphur, and oxygen in iron and steel.   Either the movement of phosphorus in iron from places of higher to places of lower concentration proceeds in accordance with some law which is more complex than Fick's law of linear diffusion, or some other factor is operating which interferes with this process.   All the curves show the same peculiar characteristics.   At the lower part where they are concave to the origin they resemble Fry's results, but the latter show no signs of the peculiar kink which occurs near the middle of all the curves in Figs. 13 and 14.

The curves shown in broken lines and lying close to the full-line curves in Figs. 13 and 14 have been calculated on the basis of a linear diffusion law, using the diffusivity constants given in the following table.   The deviation of the calculated from the experimental curves is of the

TABLE IV.

| Time. Hrs. | Temp. °C. | Diffusivity Constant $K$. | Corresponding to | |
|---|---|---|---|---|
| | | | Expt. No. | Curve. |
| $7\frac{1}{2}$ | 1000 | $1\cdot10 \times 10^{-8}$ | I. | A Fig. 13 |
| 20 | 1000 | $1\cdot15 \times 10^{-8}$ | II. | B Fig. 13 |
| 40 | 1000 | $1\cdot60 \times 10^{-8}$ | III. | C Fig. 13 |
| 80 | 1000 | $1\cdot40 \times 10^{-8}$ | IV. | D Fig. 13 |
| 80 | 950 | $0\cdot72 \times 10^{-8}$ | V. | E Fig. 14 |
| 80 | 1040 | $2\cdot50 \times 10^{-8}$ | VI. | F Fig. 14 |

same kind in all cases.   Thus it would appear that these differences are not due to any accidental or haphazard cause, but that they are governed by some fundamental factor.

A consideration of the curves in Figs. 13 and 14 shows that, for all the experiments carried out at 1000° C. the kinks occur at approximately 1·2 per cent. of phosphorus ; the corresponding points for the 950° and 1040° experiments being at 0·9 per cent. and 1·7 per cent. respectively.   Thus, it might be concluded that the concentration of phosphorus at the point corresponding to the kink in the curve is a function of the temperature, and is independent of the duration of phosphorisation within the limits of these experiments.

In this connection, a portion of Haughton's Iron-Phosphorus equilibrium diagram [8] may be considered.   The full line curves in Fig. 15 show the appropriate part of this diagram in which the area to the left of the curve FME indicates the conditions of stability of iron and its phosphorus alloys in the $\gamma$-state, whilst the region enclosed by the figure ABCDEMF indicates conditions for stability of these alloys in the $\alpha$ form. As the iron used in the present investigation contained only 0·03 per cent. of carbon, the disposition of the lines in the diagram will not be altered appreciably by such a small amount of this element.

Considering the phosphorisation made at 1000° C., it will be seen that the iron should change from the $\gamma$ to the $\alpha$ state when the concentration of phosphorus exceeds 0·4 per cent.   As the phosphorus in a large

[8] Haughton, *J. Iron Steel Inst.*, 1927, I, 417-434.

portion of the phosphorised zones of the bars used in this investigation far exceeds this figure, the solvent iron should be undergoing the $\gamma$ to $\alpha$ transformation progressively as the diffusing phosphorus causes this critical concentration to be exceeded.   Since the transition of iron from one form to another is accompanied by a complete change in all its physical properties, the rate of diffusion of phosphorus will most probably be different in the two forms.   Hence it is not surprising to find some peculiarity in the shape of the phosphorus concentration/depth curves. The positions of the kinks in these curves, where the straight and bent parts meet, are indicated by the points X, Y and Z in Fig. 15.   These
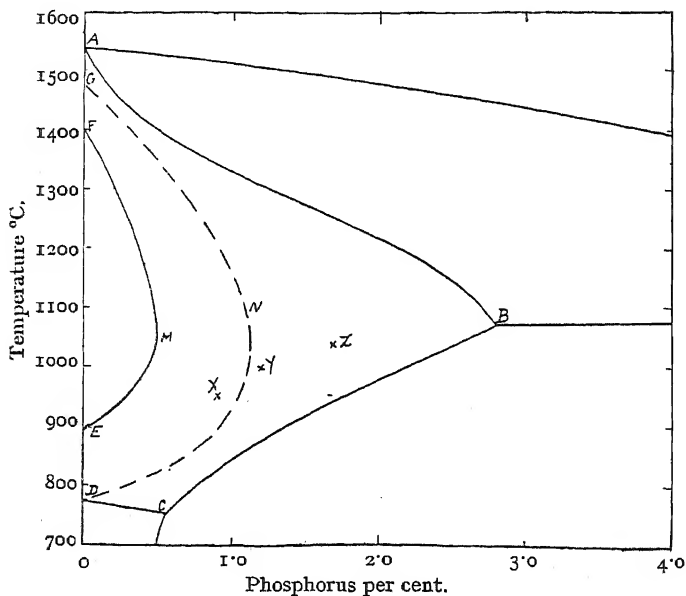


FIG. 15.—Iron-phosphorus equilibrium diagram (after Haughton).

points do not appear to be connected with any line on the diagram, although they might have been expected to fall near the curve EMF. When, however, account is taken of the extremely slow rate of transformation of the iron-phosphorus alloys (see Haughton, *loc. cit.*[8]) such differences are not surprising.

## Series E.   Phosphorisation of Carbon Steel.

A microscopic examination of transverse sections of the bars used in the foregoing experiments revealed the fact that, although the concentration of the carbon in the metal used was very low, this element had nevertheless been driven before the advancing phosphorus.   The experiments now about to be described were made in order to ascertain what effect the presence of a higher concentration of carbon would have on the diffusion of phosphorus.

The steels used were of the following compositions (Table V.)

The conditions of phosphorisation were identical with those for experiment III., and the results are shown in Fig. 16, in which the full line curves C, G, H, and I refer to experiments III., VII., VIII., and IX. respectively.

TABLE V.

|  | | | Expt. VII. | Expt. VIII. | Expt. IX. |
|---|---|---|---|---|---|
| Carbon . | . | . | 0·15 per cent. | 0·41 per cent. | 0·98 per cent. |
| Silicon . | . | . | 0·20 ,, ,, | 0·18 ,, ,, | 0·17 ,, ,, |
| Manganese | . | . | 0·30 ,, ,, | 0·30 ,, ,, | 0·25 ,, ,, |
| Sulphur | . | . | 0·024 ,, ,, | 0·025 ,, ,, | 0·022 ,, ,, |
| Phosphorus | . | . | 0·020 ,, ,, | 0·025 ,, ,, | 0·020 ,, ,, |

It is obvious that the presence of carbon has a great influence on the diffusion of the phosphorus. The broken line curves lying near C, G, and H in Fig. 16 have been calculated, using the following values of the diffusivity constants, K and assuming Fick's law of linear diffusion.

It will be apparent from the positions of the curves in Fig. 16 and the foregoing figures that not only has an increase in the con-
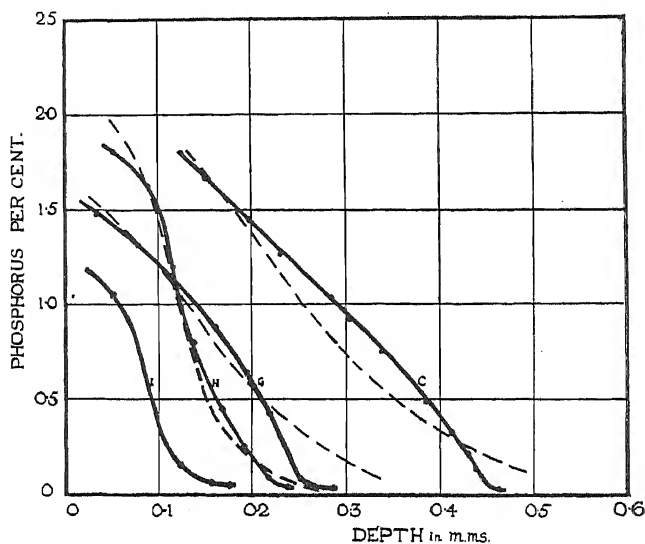


FIG. 16.—40 hours' phosphorisation at 1000° C. of
Curve C.   Experiment III.    Swedish iron.
  ,,   G.         ,,        VII.   0·15 per cent. carbon steel.
  ,,   H.         ,,        VIII.  0·41    ,,         ,,
  ,,   I.          ,,        IX.    0·98    ,,         ,,

centration of carbon a great depressing effect on the rate of diffusion of phosphorus, but the anomalies previously mentioned between the calculated and experimental curves gradually disappear with increase in carbon content. In the case of the 0·96 per cent. carbon steel, there is complete coincidence between the experimental and calculated figures.

TABLE VI.

| Expt. No. | Per Cent. Carbon in Steel. | Curve in Fig. 16. | Diffusivity Constant $K \times 10^{10}$. |
|---|---|---|---|
| III. | 0·03 | C | 16·0 |
| VII. | 0·15 | G | 7·0 |
| VIII. | 0·41 | H | 2·8 |
| IX. | 0·96 | I | 1·3 |

This gradual merging of the two curves may be explained by means of Haughton's equilibrium diagram.

It has already been stated that the area within the loop EMF, Fig. 15, indicates the region of stability of $\gamma$-iron and beyond this the stable-form is the $\alpha$-varie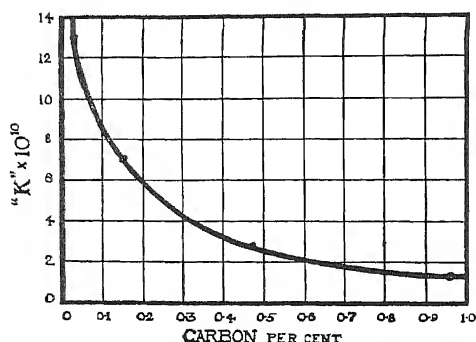ty.   The addition of carbon to iron alters the position of the points E and F ; the presence of 0·35 per cent. of this element lowers E to D and raises F to G.   On increasing the concentration of phosphorus in a steel containing 0·35 per cent. of carbon, the limit of stability of the $\gamma$ form of the metal will be extended from the position EMF to some such position as DNG, and still further to the right as the concentration of carbon increases.   It is therefore probable that, for a high carbon steel such as that used in experiment IX., the metal would retain its $\gamma$-ferrite form throughout the whole process of phosphorisation.   The suppression of the allotropic transformation by the presence of a sufficient amount of carbon removes the cause for ab-



FIG. 17.—Effect of carbon concentration on the diffusivity constant, K, for phosphorus at 1000° C.

normality, and the phosphorus concentration/depth curves become normal diffusion curves.

The effect of carbon on the diffusivity of phosphorus in steel at 1000° C. is shown by the curve in Fig. 17. For Swedish iron at this temperature, the mean of all
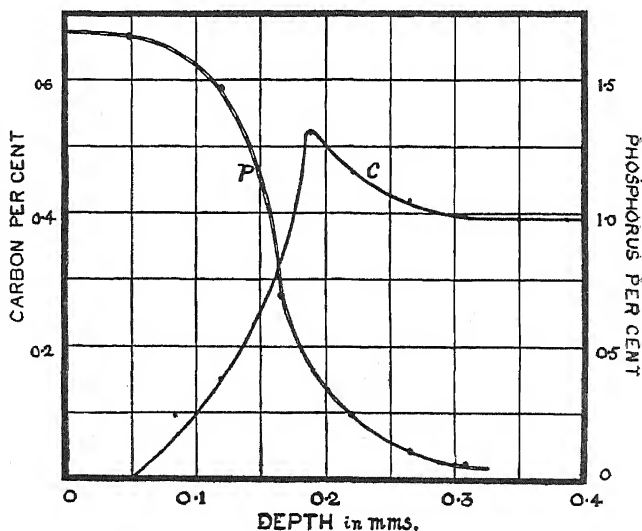


FIG. 18.

Experiment X.   Distribution of phosphorus (curve P) and carbon (curve C), resulting from 80 hours' phosphorisation at 1000° C. of a 0·4 per cent. carbon steel.

the values of the diffusivity constants deduced from the experiments of this investigation is $13 \times 10^{-10}$, a figure considerably less than one-hundredth of that for carbon.   Further, the presence of the latter element causes a lowering of this constant to such an extet that, for

steel containing 1 per cent. of carbon, it falls to $13 \times 10^{-11}$, a figure far below one-thousandth of the corresponding diffusivity constant for carbon.

It has already been stated that the advancing phosphorus drives the carbon before it in the case of a very low carbon steel, the next experiment, No. X., was made with the object of ascertaining whether the carbon is completely expelled from the phosphorised layer, and to obtain information if possible concerning a peculiar narrow band of metal which exists in the phosphorised zone near the limit of penetration of the diffusing element. The 0·40 per cent. carbon steel was used, and phosphorisation at 1000° C. was carried on for 80 hours. Both phosphorus and carbon were estimated, and the analytical results are represented by curves P and C respectively in Fig. 18. It will be seen that the carbon has not been completely eliminated from the phosphorised zone, but the peak in the carbon curve shows clearly that the entrance of the phosphorus has caused some of the carbon to be driven inwards.

## Carburisation of Phosphorised Steels.

The last series of experiments proves that carbon in steel presented a considerable obstruction to the diffusion of phosphorus. Two experiments, Nos. XI. and XII., were made to ascertain the effect of high phosphorus concentration on the diffusion of carbon. Two bars of Swedish iron were phosphorised for 40 hours at 1000° C. The thin scale of phosphide was removed by rubbing with emery cloth until a clean metallic surface was obtained and afterwards they were carburised for 10 hours, No. XI. at 1000° C. and No. XII. at 950°. Both carbon and phosphorus were estimated, and the results are indicated by curves C and P respectively
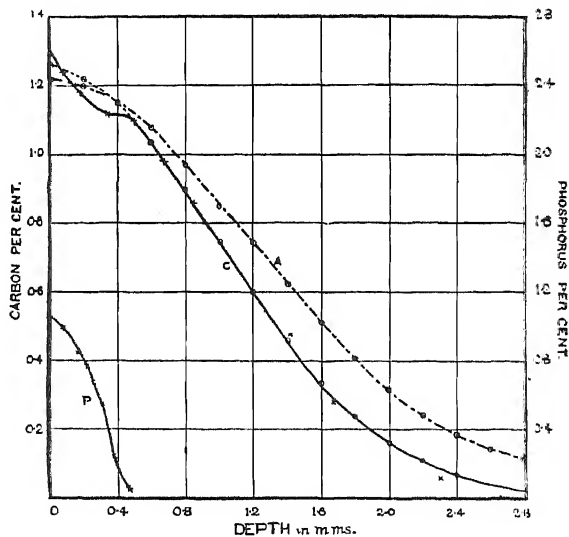


FIG. 19.

Experiment XI. Swedish iron; curve P, phosphorus; curve C, carbon resulting from 40 hours' phosphorisation at 1000° C., followed by 10 hours' carburisation at 1000° C.

in Figs. 19 and 20. The curves A in these two figures indicate the results of carburisations of the original Swedish iron under exactly the same conditions. (See Bramley and Lord.[1])

The presence of the phosphorus has had some effect on the rate of diffusion of the carbon, but it is slight, very much less than was found in the corresponding sulphur experiments. The peculiar shape of the

carbon curves at the upper end has no doubt resulted from a redistribution of this element during the period of cooling.

The diffusivity constants for carbon in the Swedish iron used were found by Bramley and Lord to be $18 \times 10^{-8}$ at 1000° C., and $12 \times 10^{-8}$ at 950° C. The circles shown on the curves C in Figs. 19 and 20 are the values calculated, using $14 \times 10^{-8}$ and $10 \times 10^{-8}$ respectively. These figures again show how little the effect has been.
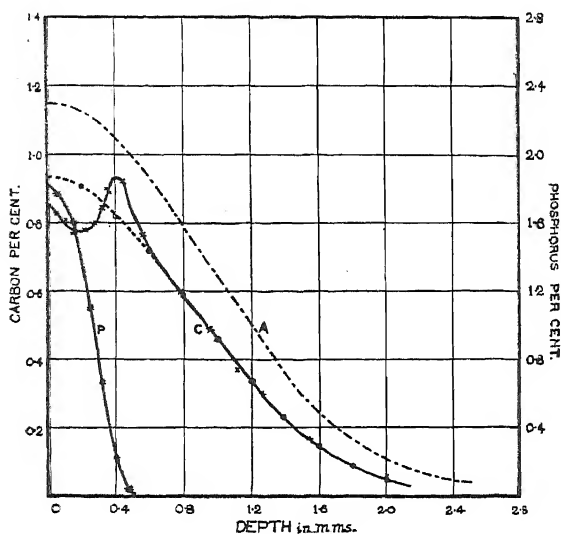


FIG. 20.

Experiment XII.    Swedish iron; curve P, phosphorus; curve C, carbon resulting from 40 hours' phosphorisation at 1000° C., followed by 10 hours' carburisation at 950°.

## Microstructures.

A thorough examination of the microstructures of all the specimens used was made, and a number of interesting features were observed.    Fig. 21 is a photomicrograph prepared from a transverse section of the bar used in experiment VI., and is typical of all the others of that series.

Before etching, the polished specimen showed radial lines near the surface indicating columnar crystals.    After etching with an alcoholic solution of picric acid, these lines became so broad, especially near the edge of the section, as to indicate definite fissures.    This was confirmed by examining the curved surface of the bar.    On polishing and etching distinct cracks could be seen ; the metal appeared to consist of polygonal crystals, the boundary lines between which had developed into cracks.

According to Bannister and Jones,[9] the conditions prevailing during these experiments would be favourable for the development of a columnar crystalline structure.    The radial lines persist to a depth indicated by arrows AA, and no other crystalline boundaries were noticeable in this zone.    This depth, 0·7 mm., in experiment VI., is the same as the limit of penetration of the phosphorus, as determined by chemical analysis. Immediately below this line the crystals are much smaller and equi-axed.

The actual splitting of the surface metal into columns of polygonal cross-section probably happened whilst the bar was cooling down after the phosphorisation was over.    Such a supposition would offer a possible explanation of the large number of parallel lines which cross each of the columnar crystals.    In a few cases two lots of parallel lines are seen on the same crystal.    These lines are evidently connected in some way with the orientation of the crystals on which they occur.

[9] Bannister and Jones, *J. Iron Steel Inst.*, 1931, 2, 71-93.

Haughton [8] found that iron phosphide is very liable to separate from a super-saturated solid solution along the cleavage planes of the crystal. The parallel lines crossing the crystals in Fig. 21 cannot be due to this, since a copper etching agent failed to produce white lines on a dark background, as shown in Haughton's paper. Further, the appearance of these lines at depths greater than that indicated by the arrows BB could not possibly be explained on the basis of phosphide separation, since the concentration of phosphorus in the alloy in that region is below the saturation value according to Haughton's results. The following suggestion is put forward to account for these lines.

During the process of phosphorisation an alloy having a greater coefficient of expansion than the original metal was formed, consequently, on cooling, great stresses would arise in the phosphorised zone and immediately below it. When these stresses became greater than the metal could withstand, rupture would take place, resulting in the formation of the radial columns already described. Simultaneously with the sudden release of these stresses, the metal would suffer a violent shock, thus giving rise to conditions favourable to the production of Neumann lines. It is suggested that the lines under consideration are Neumann lines which have been produced in this way.

The micrograph shown in Fig. 22 was prepared from a transverse section of the bar of 0·15 per cent. carbon steel used in experiment VII. This again shows columnar structure down to the limit of penetration of the diffusing phosphorus and lines crossing these columnar crystals but, with the exception of the one opposite the arrow at A, they differ from those in Fig. 21, as the lines are not straight. There is, however, a general parallelism of the lines on each individual crystal which must be connected in some way with the orientation of the latter. The micrograph, in Fig. 22, bears a striking resemblance to one given by Hindley in the discussion of Bannister and Jones's paper. In Hindley's case, arsenic had diffused into mild steel, and the Neumann lines shown in his micrograph were attributed to the effect of great pressure, and not to mechanical shock.

The micrograph, Fig. 23, was prepared from the bar used in experiment X., the etching agent used was Stead's Copper Reagent. When polishing this specimen, it was observed that a very narrow band of metal parallel to the edge of the section, and situated just inside it, had a much higher reflecting power than the rest of the surface. This is the band A in the micrograph in which its appearance contrasts sharply with that of the metal on either side of it. Comparing this micrograph with the analytical results in Fig. 18, it will be seen that the outer edge of the band coincides with the depth corresponding to the point of intersection of the phosphorus and carbon curves, and the inner edge coincides with the peak on the carbon curve. Thus it would seem that the band of metal indicated by A in Fig. 23 is a solid solution containing both phosphorus and carbon. The analytical results show that the diffusing phosphorus has reached a depth considerably greater than that of the band A.

The results of this investigation show that :—

(a) Phosphorus diffuses into iron and steel, but the distribution of this element in the phosphorised zone is peculiar, and unlike that observed when carbon, nitrogen, sulphur or oxygen is the diffusing element.

The abnormal shape of the phosphorus concentration/depth curve might be explained on the basis of an allotropic change taking place in

the solvent metal.    Haughton's Iron-Phosphorus equilibrium diagram indicates that such a change must take place during the process of phosphorisation.

(b) The rate of diffusion of phosphorus in iron is less than one-hundredth of that of carbon, and is still further lowered by the addition of carbon to the metal.

(c) Although diffusing phosphorus drives before it most of the carbon already present in a steel, the presence of relatively high phosphorus offers but little obstruction to the diffusion of carbon.

## PART IV.—THE NITRIDING OF IRON AND STEEL.*

The formation of a nitride of iron by the action of ammonia and other forms of combined nitrogen on the metal has been known for a long time.    The diffusion of nitrogen into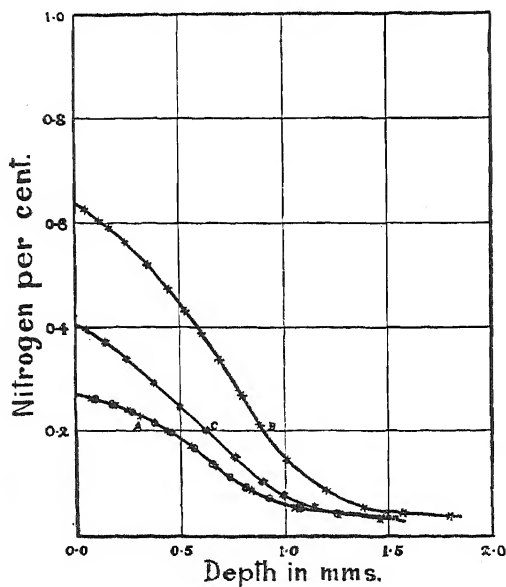 iron and steel has been studied fairly intensively during recent years by a number of workers, chief amongst whom is Fry,[10] who has developed a process with special steels for the purpose, which has become of great industrial importance.



FIG. 24.

A.   Experiments I. and II. . Swedish iron nitrided at 900° C. for 20 hours.
B.   Experiments III.    Armco iron nitrided at 900° C. for 20 hours.
C.   Experiments IV.    Mild steel nitrided at 900° C. for 20 hours.

Using plain carbon steels containing no other alloying elements, Bramley and his co-workers [1] have shown that the movement of the nitrogen in the metal follows the ordinary laws of linear diffusion. It has been found, however, in the work about to be described, that small quantities of oxygen, either free in the nitriding atmosphere, or combined as iron oxide dissolved in the metal itself, has a remarkable effect on the rate of formation of iron nitride and the diffusion of this element into the metal.

Unlike the cases described in Parts I., II., and III., in which the presence of sulphur, oxygen, or phosphorus has a depressing action on the amount of carbide formed, and lowers the rate of diffusion of the latter in steel, it has been found that both the quantity of nitride produced

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* By Arthur Bramley and John Thomas Watts.
[10] Fry, *Krupp's Monat.*, 1923, 4, 137.

and its rate of diffusion in the metal is increased by the presence of a limited amount of oxygen or iron oxide.

The method of experiment first used was the same as that described by Bramley and Beeby.[1]  Bars of Swedish charcoal iron were nitrided and the distribution of the nitrogen afterwards determined by chemical analysis. The results differed considerably from those obtained formerly, and the research now about to be described consisted of a careful investigation into the causes of these differences.

Nitrogen, from a cylinder of the commercial gas, was carefully freed from oxygen by passing through a double tube furnace containing rolls of copper gauze at about 800° C.  The gas was then passed in the form of small bubbles through strong aqueous ammonia, and the issuing gas thoroughly dried by passing over freshly ignited calcium oxide. The mixture thus obtained, consisting of approximately equal volumes of nitrogen and ammonia gas, was led through the tube furnace containing the bars of metal to be acted upon.  Four experiments, carried out as nearly as possible in the same way, were made in order to test the accuracy with which the results could be reproduced.  The nitriding was done with the bars at a temperature of 900° C. for 20 hours.  The analytical results of these experiments are represented by the curve A, Fig. 24, the circles indicating the figures from experiment I. and the crosses from experiment II. The other two experiments give practically identical results, and their reproducibility was thus established.
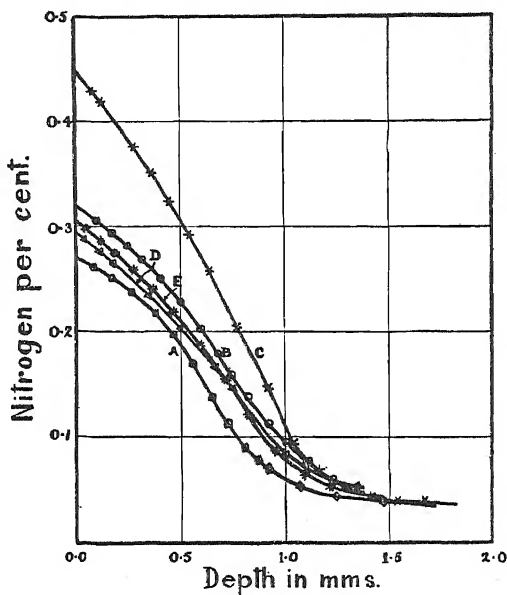


FIG. 25.—Swedish iron nitrided for 20 hours at 900° C.

Curve A.  Experiments I. and II.  Nitrided with nitrogen and ammonia.
Curve B.  Experiment V.  Nitrided with nitrogen containing 1 per cent. oxygen and ammonia.
Curve C.  Experiment VI.  Nitrogen containing 2 per cent .oxygen and ammonia.
Curve D.  Experiment VII.  Nitrogen containing 3 per cent. oxygen and ammonia.
Curve E.  Experiment VIII.  Nitrogen containing 5 per cent. oxygen and ammonia.

The curves B and C in the same figure were obtained by the nitriding of Armco iron and a mild steel (0·15 per cent. carbon) under the same conditions.  Obviously, the composition of the metal is one factor influencing the extent of nitride formation.

## Effect of the Presence of Free Oxygen in the Nitriding Atmosphere.

Four experiments, Nos. V. to VIII., were made in which the same Swedish charcoal iron was used.  The temperature and period of nitriding was the same as for experiments I. and II., but to the nitriding atmosphere

was added 1, 2, 3, and 5 per cent. by volume of oxygen in experiments V. to VIII. respectively. The analytical results of these experiments are shown graphically by the curves B, C, D, and E respectively in Fig. 25. The curve A, representing the corresponding experiment made without oxygen, is included for comparison. Obviously the addition of oxygen to the nitriding atmosphere has increased the amount of nitride formed, the optimum effect being produced by the presence of about 2 per cent. of this element.
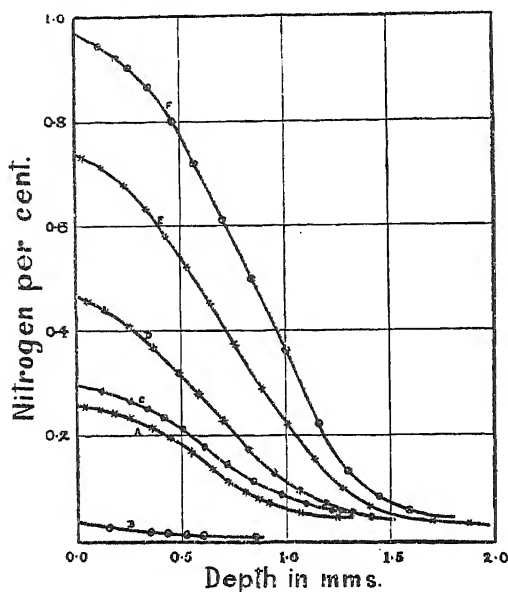


FIG. 26.—Swedish iron.

Curve A. Experiments I. and II. Original Swedish iron.
Curve B. Experiment IX., 10 hours' oxidation, 1000° C. (50 per cent. CO, 50 per cent. $CO_2$).
Curve C. Experiment X, 10 hours' oxidation, 1000° C. (75 per cent. CO, 25 per cent. $CO_2$).
Curve D. Experiment XI., 30 hours' oxidation, 1100° C. (75 per cent. CO, 25 per cent. $CO_2$).
Curve E. Experiment XII., 100 hours in a malleablising furnace.
Curve F. Experiment XIII., 200 hours in a melleablising furnace.

Attention has been previously drawn by Cunningham and Ashbury [11] to the presence of temper colours on nitrided steels ; they state that the nitride case suffers no deleterious effect on that account. It will be shown later, however, that if the atmosphere is so strongly oxidising as to produce microscopic crystals of iron oxide on the surface of the steel, nitriding is completely inhibited.

The maximum concentration of nitrogen indicated by curve C, Fig. 25, is well below that produced in the surface of Armco iron, as shown in curve B, Fig. 24. Hence, some other and more potent factor must be operative in the latter case. This factor was next considered.

## Effect of Dissolved Oxide in the Metal.

In a previous section it was ascertained that the concentration of oxygen in the Swedish iron and Armco iron used in these experiments was 0·04 and 0·09 per cent. respectively. Since the other constituents in these two metals do not differ much in concentration, and are not likely to affect the amount of nitride formed, the remarkable difference in their reaction towards the nitriding process must be attributed to the presence of the dissolved oxide. If this is the case, it should be possible, by subjecting the Swedish iron to a certain degree of oxidation before nitriding, to increase its reactivity towards the latter operation.

[11] Cunningham and Ashbury, *J. Iron Steel Inst.*, 1931, 124, II, 215-228.

In experiment IX., a bar of the Swedish iron was heated for 10 hours to 1000° C. in a steady stream of a mixture of equal volumes of carbon monoxide and carbon dioxide. This treatment caused a certain amount of oxidation to take place ; the bar was found to have a fine frosted appearance, the surface being covered with minute crystals of iron oxide, visible under a low power microscope. The quantity of oxide formed was not sufficient to produce a scale. This bar was then nitrided under the same conditions as experiments I. and II., with the result shown by curve B in Fig. 26. Curve A in this figure, from experiments I. and II., is added for comparison. Obviously, nitride formation has been completely inhibited by the previous treatment.

Experiments X. and XI. were made on similar lines, but the degree of oxidation was so far restricted as to avoid the production of any free oxide. Subsequent nitriding yielded the results depicted by curves C and D in Fig. 26. In the latter case, the amount of nitride formed is
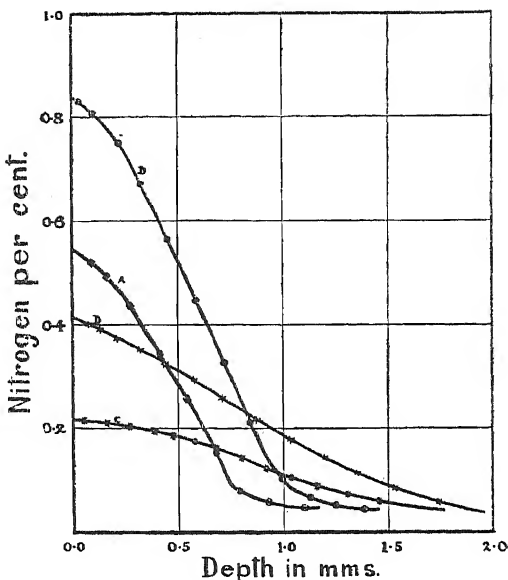


FIG. 27.

Curve A.  Experiment XIV.  Swedish iron nitrided at 850° C.
Curve B.  Experiment XV.  Armco iron nitrided at 850° C.
Curve C.  Experiment XVI.  Swedish iron nitrided at 950° C.
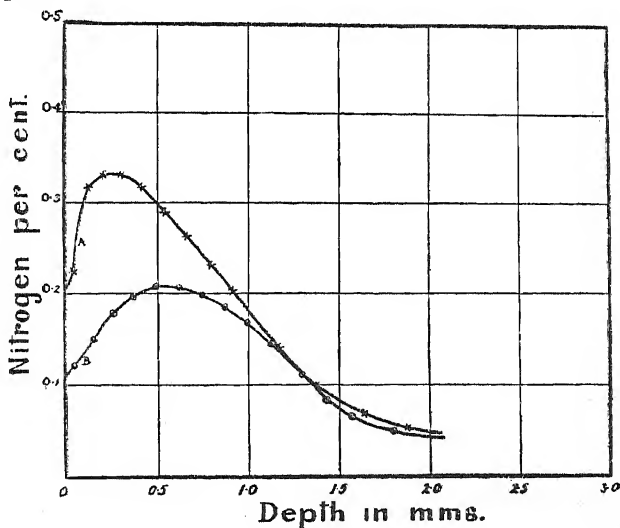Curve D.  Experiment XVII.  Armco iron nitrided at 950° C.



FIG. 28.

Curve A.  Experiment XVIII.  Swedish iron nitrided for 40 hours at 900° C.
Curve B.  Same bar after 5 hours' reheating at 900° C.

about double that produced in the original untreated iron.    In experi-
ments XII. and XIII., portions of the bars of Swedish iron which had
been heated in a white-heart malleablising furnace for 100 and 200 hours
respectively, were used.    All traces of free oxide and superficial corrosion
were removed by rubbing with emery paper before nitriding.    The con-
centration of oxygen in these bars before subjecting to the latter process
is shown by curves C and D respectively in Fig. 7, Part II. and the effect
of nitriding by curves E and F, Fig. 26.    The higher concentration of
oxide has increased the amount of nitride three- and four-fold in these
two experiments.

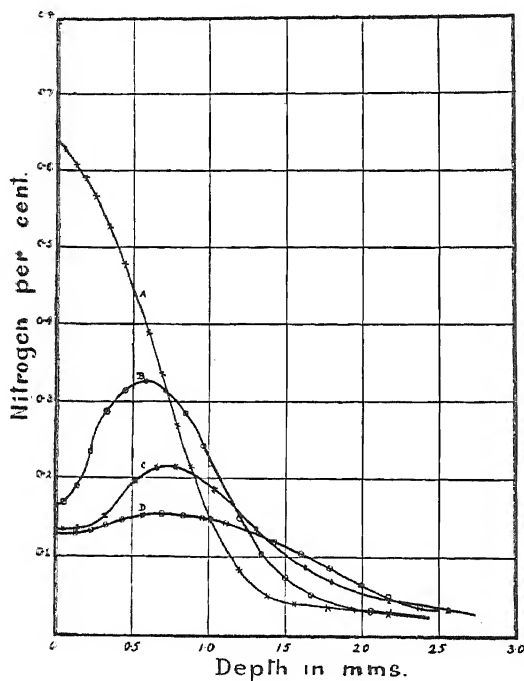All the nitriding operations in the foregoing experiments were conducted
at 900° C.    Compara-
tive tests with the
Swedish iron and the
Armco iron were made
by nitriding at 850°
and 950° C.    The re-
sults shown in Fig. 27
indicate the same kind
of difference in the
behaviour of the two
metals.

Previous work has
shown that iron nitride
is not very stable at
high temperatures, and
the next experiments
were made to ascertain
whether its stability
was affected in any
way by the concentra-
tion of oxygen in the
metal.

In experiment
XVIII. a bar of the
Swedish iron was ni-
trided for 40 hours at
900° C.    Half of the
bar was reheated at
900° C. for 5 hours in
an atmosphere of hy-
drogen with the results
shown in Fig. 28.
Similar experiments
were made with Armco
iron, the curves given
in Fig. 29 showing the
effect of reheating for
various periods in an
atmosphere of hydro-



FIG. 29.

Curve A.    Experiment XIX.    Armco iron nitrided
    for 20 hours at 900° C.
Curve B.    Experiment XX.    Reheated for 5 hours
    at 900° C.
Curve C.    Experiment XXI.    Reheated for 20 hours
    at 900° C.
Curve D.    Experiment XXII.    Reheated for 40 hours
    at 900° C.

gen.    A comparison of the curves in Figs. 28 and 29 leads to the con-
clusion that iron nitride is much more stable when present in Armco iron
than in the Swedish iron.

An attempt was made to remove the oxygen as completely as possible
from the surface metal of the Swedish iron in order to ascertain the effect
of nitriding an iron free from oxide.    In experiment XXIII. a bar of the
Swedish iron was heated to 1050° C. for 200 hours in a steady current of
carefully dried hydrogen, and immediately afterwards nitrided under the
same conditions as experiments I. and II.    The effect of this treatment,
which must have reduced the concentration of oxygen near the surface

very considerably, is shown in Fig. 30, curve B.   Curve A from experiments I. and II., is included for comparison as is also curve D from experiment XI., in which approximately the same amount of nitride was produced as in experiment XXIII.

Judging by the results of the previous experiments, the effect of the preliminary treatment with hydrogen should have been to decrease rather than increase the amount of nitride formed, whereas the opposite has been the case.

Although the amount of nitride produced in experiments XI. and XIII. was about the same in both cases, there is, as the slopes of the curves B and D in Fig. 30 indicate, an important difference in its distribution which will be further considered below. The unexpectedly large amount of nitride formed in experiment XXIII. may be due entirely to the increased sensitivity of the surface metal brought about by the reducing action of the hydrogen.



FIG. 30.

Curve A.   Experiments I and II.   Swedish iron nitrided for 20 hours at 900° C.

Curve B.   Experiment XXIII.   Swedish iron, reduced for 200 hours in a current of dry hydrogen, and then nitrited.

Curve D.   Experiment XI.   Swedish iron oxidised for 30 hours and then nitrited.

In the earlier work of Bramley and his co-workers,[1] in which it was shown that the movement of carbon and nitrogen in iron and steel took place in accordance with Fick's law of linear diffusion, the following expression, which is a solution of Fick's equation, was used :—

$$\phi = \frac{H}{\sqrt{4\pi kt}} \cdot e^{-\frac{x^2}{4kt}}$$

in which $\phi$ = concentration of nitrogen above that initially present in the steel at a depth $x$ below the surface,

$t$ = time during which diffusion was taking place,

$k$ = diffusivity constant,

$H$ = a constant depending on the concentration of nitrogen at the surface of the metal.

This relationship has been applied to the results of this investigation in order to ascertain how the diffusivity constant $K$ is affected by the concentration of oxygen in the metal subjected to nitriding.

By taking any two points on a nitrogen concentration/depth curve and substituting the corresponding values of $\phi$ and $x$ in the above
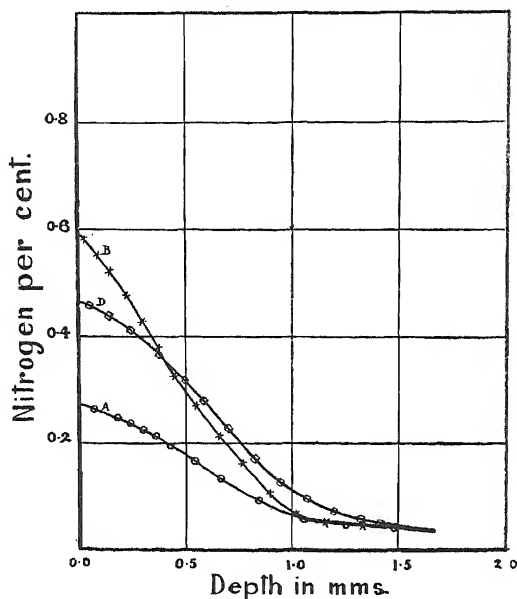
equation, $H$ can be eliminated and the value of $K$ is then given by the expression

$$K = \frac{(x_2^2 - x_1^2) \log e}{4t \log \dfrac{\phi_1}{\phi_2}}.$$

TABLE VII.

| Expt. No. | Condition or Treatment of Iron, Prior to Nitriding. | Diffusivity Constant $K \times 10^8$. |
|---|---|---|
| XXIII | Swedish Iron heated for 200 hrs. at 1050° C. in dry hydrogen. . . . . . . | 1·8 |
| I and II | Swedish Iron in its original state. . . . | 2·1 |
| XI | Swedish Iron oxidised for 30 hrs. in a 75-25 per cent. mixture of CO and $CO_2$. . . . | 2·5 |
| III | Armco iron in its original state. . . . | 2·6 |
| XII | Swedish Iron oxidised for 100 hrs. in a malleablising furnace at 1000° C. . . . . | 2·9 |
| XIII | Swedish Iron oxidised for 200 hrs. in a malleablising furnace at 1000° C. . . . . | 3·5 |
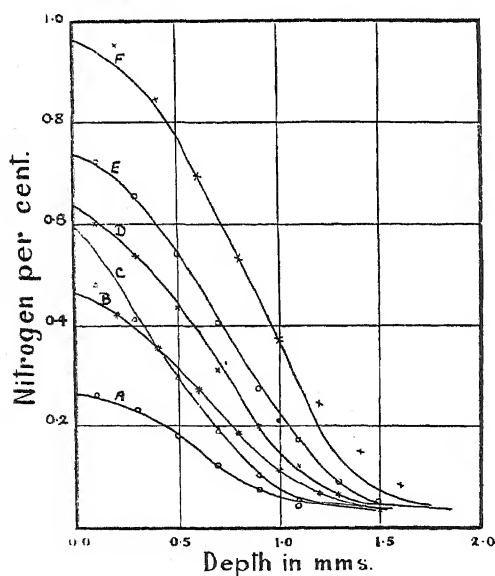


FIG. 31.

| Curve | Experiments | | | |
|---|---|---|---|---|
| A. | I. and II. | Analytical results | | o |
| B. | XI. | ,, | ,, | * |
| C. | XXIII. | ,, | ,, | Δ |
| D. | III. | ,, | ,, | × |
| E. | XII. | ,, | ,, | o |
| F. | XIII. | ,. | . | + |

This has been done for a number of cases and the corresponding values of $K$ found are given in Table VI., together with other particulars of the experiments which are pertinent to the problem. In each case the nitriding operation was carried out at 900° C.

Using the values for $K$ given in the foregoing table, the positions of the curves approximating most closely to the experimental figures have been calculated. These calculated curves are shown in Fig. 31. The experimental points, indicated by the various symbols, will show the nature of the agreement. In four cases, A, B, D, and E, this is perfect, but it is not so good in C and F. It should be noted, however, that the

metal into which diffusion of the nitrogen is being studied, is only homogeneous in two cases, A and D. The preliminary treatment in the other cases must have resulted in producing a certain degree of heterogeneity near the surface, and this will be greatest in the two cases C, and F, in which the discrepancies between the calculated and observed points are most marked.

The details in the foregoing table show quite clearly that the diffusivity constant $K$, for nitrogen in iron increases progressively with the degree of oxidation of the latter. The apparently contradictory result of experiment XXIII. is now explained. Since the reduction of the oxygen in the metal, prior to nitriding, has resulted in a corresponding fall in the diffusivity constant, the relatively large amount of nitride formed must be due entirely to the improved activity of the surface metal.

The part played by oxygen in increasing both the amount of nitride formed and its rate of diffusing into the metal is somewhat obscure, but the following is put forward as a possible explanation :—

($a$) Reaction between the ammonia and iron takes place at the surface of the metal in accordance with the equation

$$4Fe + 2NH_3 = 2Fe_2N + 3H_2.$$
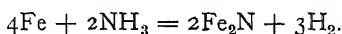
($b$) The iron nitride formed dissolves in the iron itself, which is in large excess, forming a solid solution. In this solution partial dissociation takes place as per the equation

$$Fe_2N \rightleftharpoons 2Fe + N,$$
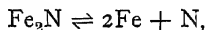
and a balanced action results.

The fate of the nitrogen thus liberated in the atomic form may be varied. On account of the concentration gradient of nitrogen which must decrease towards the interior of the metal, some of this element will diffuse inwards. Whilst still in the atomic state, reaction will take place between the nitrogen and other iron atoms situated at a greater depth than those from which it was previously liberated, and diffusion will proceed accordingly. On the other hand, two such atoms of nitrogen coming together would form a molecule which, being inactive towards iron, would ultimately escape from the metal. During the process of nitriding this loss of nitrogen is more than counterbalanced by the supply of fresh nitride from the surface of the metal.

The presence of oxygen in the metal, whether free or as dissolved iron oxide, offers a third method of disposing of the atomic nitrogen. Some oxide of nitrogen, probably nitric oxide, may be formed which, although having only a transitory existence, reacting almost immediately afterwards with the iron, would in the interim prevent the nitrogen from passing into the inactive molecular form, and subsequently escaping from the metal.

The very marked effect of the greater concentration of oxygen in the Armco iron in retarding the loss of nitrogen when the nitrided metal was heated lends strong support to this view.

## Summary.

(1) Preliminary experiments indicated that the degree of nitriding of iron by heating in an atmosphere of ammonia, depended upon the presence or absence of small quantities of oxygen in the nitriding atmosphere or of dissolved oxide in the metal.

(2) Experiments have been made in which the concentration of oxygen in the nitriding atmosphere was varied, and it has been found that the optimum effect was obtained with approximately 2 per cent. of this element.

(3) Restricted oxidation of the metal has been found to have a marked effect on the degree of nitriding, the latter increasing rapidly with the amount of dissolved oxide in the metal. If, however, the preliminary oxidation of the metal has resulted in the production of the slightest trace of microscopic crystals of iron oxide on the surface, nitriding in an atmosphere of ammonia is completely inhibited.

(4) The rate of diffusion of the nitrogen has been found to depend on the concentration of dissolved oxide in the metal, the diffusivity constant being greater the higher the concentration of dissolved oxide.

# ON THE BOND ENERGIES AND VALENCY ANGLES IN SOME SIMPLE CARBON COMPOUNDS.

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One of the most interesting quantities which enters into any theory of molecular structure is that of bond energy. Making the assumption that bond energies are additive and that the energy of a bond between two atoms of a polyatomic molecule is the same whatever the other atoms of the molecule may be, it is possible to build up a system of values from which can be predicted the energy of formation of any molecule. Agreement with experiment is usually striking. In an important series of papers Pauling [1] has shown that bond energies should be approximately additive, or what comes to the same thing, small variations in the energy of a particular bond are to be expected, depending on the particular polyatomic molecule under consideration. In a very recent article, Serber [2] has again gone into the question as to whether the additivity of bond energy has any exact theoretical significance, and concludes that it does not. Particularly is this the case when multiple bonds are concerned.

In the following paper we consider some aspects of the C—H bond in some simple hydro-carbons, notably $CH_4$, $CH_3$ and $C_2H_2$, discussing at the same time the relative C—H distances, the heat of the reaction $CH_4 \rightarrow H + CH_3$, and the shape of the free $CH_3$ radical in its most stable configuration. The method depends on deriving a formula by the electron-pair theory for the variation of the energies of the molecules with their bond angles, the exchange integrals being regarded as parameters which are to be determined from the observed vibrational frequencies. Finally we discuss the related problem of estimating the valency angles in compounds of the type $CH_3G$, $CH_2G_2$, $CHG_3$, where G is a mono-valent system, and shall prove that remarkably little deviation from the tetrahedral angle can occur.

[1] Pauling, *J. Am. Chem. Soc.*, 1931, **53**, 1367, and subsequent papers.
[2] Serber, *J. Chem. Physics*, 1935, **3**, 81.

## The Formula of Perfect Pairing.

The well-known formula of perfect pairing for the energy of formation of a polyatomic molecule is

$$W = Q + \Sigma_i J_{ii} - \tfrac{1}{2}\Sigma'_{ij} J_{ij}, \qquad . \qquad . \qquad . \quad (1)$$

where $Q$ is the Coulomb energy and the $J$ are exchange integrals. The formula is usually regarded as a generalisation of the expression for the energy of an $H_2$ molecule. Thus the term $\Sigma_i J_{ii}$ represents the sum of the energies of the bonds, and the remaining term the interactions between them. At first sight (1) would appear to be, at the best, only a crude approximation to the actual energy of the molecule, because when the calculations are " improved " by allowing for non-orthogonality and triple permutations in the usual way, the corrections are of alarming size. The shapes of quite a number of simple molecules have been determined by an application of (1), choosing the angular parameters to minimise the energy $W$. It is therefore of some importance to see that although (1) is a bad approximation to the energy, its application to determine the shapes of molecules is valid.

Consider an assembly of atoms consisting, for example, of one carbon atom with four hydrogen atoms arranged more or less at random around it. The energy of the system can be regarded as made up of two terms, one depending merely on the distances of the H atoms from C, and the other depending on their distribution around C. We notice that the potential energy given by (1) has exactly the right form, and remember that it does represent, possibly with poor approximation, the potential function of the molecule. Now suppose that the molecule, in its equilibrium position, suffers a small displacement in which the H atoms are moved on their own sphere. The experimental evidence on the infra-red spectrum of the molecule permits a determination of the force constants for such a displacement. In other words, the experimental evidence can be used to fix the second derivatives of $W$ with respect to angular displacements of the H atoms on their sphere. These derivatives may also be calculated from (1) and turn out to be combinations of exchange integrals. Hence if these combinations of exchange integrals are determined to agree with the second derivatives of $W$, obtained from experimental evidence, the formula (1) is no longer quite what it purports to be. The exchange integrals have been adjusted so that (1) gives the correct variation of the actual energy of the molecule for small angular displacements from equilibrium. We are now dealing with effective exchange integrals, that is, quantities whose leading terms are still exchange integrals, but modified to allow for ionic and Van der Waals forces, non-orthogonality and the like. The vibrational frequencies do not determine a particular effective exchange integral, but require that a simple combination of them should have a certain numerical value. It is clearly a satisfactory approximation to assume that the ratios of the effective exchange integrals are the same as the exchange integrals obtained by quadrature. With this assumption one can then obtain a set of exchange integrals, and the substitution of these in (1) should give a very good representation of the energy of the molecule with the angular parameters.

The magnitudes of the more important effective exchange integrals obtained by the above process approximate quite closely to those obtained by quadrature alone. Thus, for example, according to (1) and

the calculated exchange integrals, the energy needed to displace an H atom off its bond line is determined mainly by $N_{\sigma\sigma}$. The force constant for such a displacement is practically the same through a series of compounds and leads to an effective value of $N_{\sigma\sigma}$ of about 2 or 2·5 e.v. Just about the same value for $N_{\sigma\sigma}$ is obtained by quadrature. It should be noticed, however, that the result obtained by quadrature depends a good deal on the value adopted for the effective nuclear charge of the central atom. The choice of this nuclear charge is influenced to a certain extent by the requirement that the energies of some simple diatomic hydride molecules come out about right, and this in turn implies that $N_{\sigma\sigma}$ has to be about 2 or 2·5 e.v. We are therefore inclined to locate the importance of a calculation of the type performed by Van Vleck and Cross [3] on the bending frequency in $H_2O$ mainly in the fact that, in combination with the criterion of maximum overlapping, or more precisely with actual numerical quadrature, it gives a method of determining the effective exchange integrals. These can then be used to express the variation of the potential energy of the molecule with its angular parameters.

According to our viewpoint, only by accident can the formula (1) give a value of the heat of formation of a molecule correct to within 30 or 40 per cent. and, in especially bad cases, may be even more in error than this. Even the most elaborate calculations, however, have up to the present failed to give anything much better. It is true that in certain cases (1) will be a much more favourable approximation than in others. Methane should be one of the best because here the ionic energy, not envisaged at all in (1), is fairly small, and, apart from the $(1s)^2$ shell, all the C electrons enter into bonds. On the other hand, the application of (1) to water can only by the greatest coincidence give anything like the true energy, because this time the ionic energies are considerable. Moreover, only two electrons of the 2-quantum orbit of O enter into bonds, and the remaining four badly complicate the problem.

To sum up, the formula (1) as a valid approximation to the energy of formation of a molecule is a poor one. Nevertheless, it should give the variation of the energy with the angular parameters rather well, provided that it is possible to get a check on the exchange integrals from the observed vibrational frequencies of the molecule.

## The Frequency $\nu_2$ of Methane.

We have made the suggestion that the experimental values of the perpendicular vibrations in certain molecules can be used to determine accurate values for the exchange integrals. In the present section we show that one of the perpendicular frequencies of methane can be used to obtain some the fundamental C—H exchange integrals.

Miss Rosenthal [4] has considered the potential energy $V$ of methane in terms of the mutual displacements of the atoms, and has shown that the most general quadratic form consistent with geometrical symmetry has only five independent parameters. The methane molecule possesses four fundamental modes of vibration and in one of these $(\nu_2)$, the C atom remains stationary and the C—H distances do not alter.

[3] Van Vleck and Cross, *J. Chem. Physics*, 1933, **2**, 357.
[4] Rosenthal, *Physic. Rev.*, 1934, **45**, 538 ; *ibid.*, 1934, **46**, 730 ; *ibid.*, 1935, **47**, 235.

This is the frequency which we can calculate. The potential function given by Miss Rosenthal reduces in this special type of displacement to

$$\delta V = \tfrac{1}{2}k_1\{\delta q_{12}^2 + \delta q_{13}^2 + \delta q_{14}^2 + \delta q_{23}^2 + \delta q_{24}^2 + \delta q_{34}^2\}$$
$$+ \tfrac{1}{2}k_2\{\delta q_{12}\delta q_{34} + \delta q_{13}\delta q_{24} + \delta q_{14}\delta q_{23}\}, \quad (2)$$

where, for example, $\delta q_{12}$ is the change in the $H_1H_2$ distance from its equilibrium value. The frequency of the vibration $\nu_2$ is given in terms of the force constants $k_1$ and $k_2$ by the equation

$$\nu_2^2 = (k_1 + \tfrac{1}{2}k_2)/4\pi^2 m, \quad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \quad (3)$$

where $m$ is the mass of the hydrogen atom. Thus $(k_1 + \tfrac{1}{2}k_2)$ can be calculated directly from the observed value of $\nu_2$. The question is thus to determine the relation between $(k_1 + \tfrac{1}{2}k_2)$ and the quantities entering into the directed valency theory. Fortunately this is a simple matter. Let us choose the variations $\delta q$ in such a way that $\delta V$ is proportional to $(k_1 + \tfrac{1}{2}k_2)$, and evaluate the expression for $\delta V$ for these same displacements from the directed valency theory. Then the required relation is obtained by equating the coefficients of the arbitrary displacements in the two expressions for $\delta V$. Consider the sphere of centre C passing through four points $H_1$, $H_2$, $H_3$ and $H_4$. Make the following displacements on the surface of the sphere. Move $H_1$ towards $H_2$ through an angle $\theta$, and then move $H_2$ towards $H_1$, also through an angle $\theta$. Make similar displacements on the pair $H_3H_4$, moving them both through angles $\theta$ towards each other.[5] Then simple geometrical arguments give

$$\delta q_{12} = \delta q_{34} = -2\delta q_{13} = -2\delta q_{14} = -2\delta q_{23} = -2\delta q_{34} = -2r\theta/(3)^{\frac{1}{2}},$$

where $r$ is the radius of the sphere and is, of course, the C—H distance in $CH_4$.

Equation (2) reduces in this case to

$$\delta V = 2r^2\theta^2(k_1 + \tfrac{1}{2}k_2),$$

and by using the relation (3), this in turn becomes

$$\delta V = 8\pi^2 m r^2\theta^2\nu_2^2. \quad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \quad (4)$$

We have now to evaluate the change $\delta V$ in the potential energy from the theory of directed valency. For the moment let us neglect the H—H repulsions. The tetrahedral orbit $i$ which forms a bond with the atom $H_i$ can be written

$$\psi_i = \{(3)^{\frac{1}{2}}\psi_C(2p\sigma_i) + \psi_C(2s)\}/2.$$

When $H_i$ is displaced by a small angle $\theta$ off the axis of symmetry of $\psi_i$, a small change in the bond energy occurs. By resolving the $2p\sigma_i$ wave function along and perpendicular to $CH_i$, and evaluating the new bond energy by the usual methods, it is found that the change in bond energy is given by

$$\delta J_{ii} = \theta^2\{3(N_{\sigma\sigma} - N_{\pi\pi}) + (3)^{\frac{1}{2}}N_{s\sigma}\}/4.$$

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[5] There are two other types of displacement similar in character to that which we have described, one where $H_1$ and $H_3$ move together, and another where $H_1$ and $H_4$ move together. Only two of the three are independent, and thus $\nu_2$ is doubly degenerate. The evaluation of $\delta V$ for any displacement which is not a simple superposition of two of these independent displacements is a complicated business, because one has to allow the directed bonds to follow their H atoms to some extent.

We have still to evaluate the change in energy due to the slightly altered interaction of $H_i$ with the other tetrahedral C orbits. It is found that

$$\underset{j,\,j\,\neq\,i}{\Sigma}\ \delta J_{ik} = -\ \delta J_{ii}.$$

Using these values in (1) to find the total change in the energy of the molecule due to the particular displacements which we have described, it is found to be given by

$$\delta V = \theta^2\{9(N_{\sigma\sigma} - N_{\pi\pi})/2 + 3(3)^{\frac{1}{2}}N_{s\sigma}/2\} + R\theta^2, \qquad . \quad (5)$$

where $R$ represents the change in potential energy arising from H—H repulsions.

If $M(x)$ is the function giving the mutual energy of two H atoms in methane which are at distance $x$ apart, we have for $R$

$$R = 2r^2\left(\frac{\partial^2 M}{\partial x^2}\right)_0,$$

the derivative being evaluated at the equilibrium H—H distance, namely $1.79 \times 10^{-8}$ cm. According to Eyring and Polanyi [6] the function $M(x)$ is in electron volts.

$$M(x) = 1.3 - 1.3[1 - e^{1.85(0.75-x)}]^2 \quad . \qquad . \qquad . \quad (6)$$

where $x$ is in Angstroms.

We have succeeded in expressing $\delta V$ in two ways, (4) and (5), and the wo expressions must be identical. Therefore

$$8\pi^2 m r^2 \nu_2{}^2 - 2r^2\left(\frac{\partial^2 M}{\partial x^2}\right)_0 = 9(N_{\sigma\sigma} - N_{\pi\pi})/2 + 3(3)^{\frac{1}{2}}N_{s\sigma}/2.$$

Inserting the numerical values of the quantities on the left hand side of this equation, and using the experimental result that $\nu_2 = 1520$ cm.$^{-1}$, it is found that the first term has the value 20·47 e.v., and the second has the value 2·20 e.v. The exchange integrals must therefore be such that

$$3(N_{\sigma\sigma} - N_{\pi\pi}) + (3)^{\frac{1}{2}}N_{s\sigma} = 12.2 \text{ e.v.}$$

Of the three integrals involved in this relation $N_{\pi\pi}$ is known quite accurately to be $-0.6$ e.v., and $N_{\sigma\sigma}$ is known to be between 2·0 and 2·3 e.v. The integral $N_{s\sigma}$ is also about 2 e.v., and from overlapping considerations would be expected to be a little less than $N_{\sigma\sigma}$. If we take $N_{\sigma\sigma}$ as 2·2, then from the above relation we obtain $N_{s\sigma}$ as 2·1. There is still one integral $N_{ss}$, which we need and for this we take the value given by Van Vleck,[7] namely 2·0. Our estimate, in electron volts, for the four fundamental C—H exchange integrals is then

$$N_{\pi\pi} = -0.6,\ N_{\sigma\sigma} = 2.2,\ N_{s\sigma} = 2.1,\ N_{ss} = 2.0. \qquad . \quad (7)$$

It is worth noticing that the above estimate of $N_{s\sigma}$ is appreciably larger than the value 1·0 e.v., given by Van Vleck. His method of determining it was to make the energy of formation of CH exactly one quarter of that of $CH_4$. We refer the reader to his paper for the details ; the main difficulties arise because the C configuration is $s^2p^2$ in one case and $sp^3$ in the other. Moreover, the energy of formation of CH is known only very roughly to be 92 Cals. Recent work of Price [8] strongly suggests

[6] Eyring and Polanyi, *Z. physik. Chem.*, 1931, **12**, 279. As is usual now, we use 30 per cent. Morse function instead of 35.
[7] Van Vleck, *J. Chem. Physics*, 1933, **1**, 177, 219 ; *ibid.*, 1934, **2**, 20, 297.
[8] Price, *Physic. Rev.*, 1934, **45**, 843.

that the energy needed to dissociate $C_2H_2$ into two normal CH radicals is 187 Cals., and if this is the case, the energy of formation of CH must be about 80 Cals. As we have explained, (7) are effective exchange integrals, chosen to fit the force constants, and do not necessarily give the correct value for the total energy.

### The Methyl Radical.

Our remarks on the free methyl radical can be divided into three sections. The first shows that experimental evidence alone indicates that the shape of the free radical in its most stable form is not the same as that of a $CH_3$ group in methane. The second demonstrates from general considerations that the most stable configuration of the radical is a plane one, a possibility previously suggested by Van Vleck.[7] The third section gives an estimate of the heat of the reaction $H + CH_3 \rightarrow CH_4$ from the directed valency theory.

### Section 1.

The energy of formation of methane from normal atoms can be regarded as composed of parts, as shown in the formula

$$W(CH_4) = 4x - V(v) - 6M(H_2). \qquad . \qquad . \qquad . \quad (8)$$

Here $x$ represents the actual energy of binding of an H atom to the central C atom, and is, of course, considerably greater than the net energy $W(CH_4)/4 = 93 \cdot 5$ Cals. of the C—H bond of methane. The quantity $V(v)$ represents the promotional energy it is necessary to give the normal $^3P$ carbon atom to get it into the valency state in which it exists in the methane molecule, and $6M(H_2)$ represents the six pairs of steric repulsions between the hydrogen atoms. The quantity $V$ can be calculated accurately from spectroscopic data, as has been shown by Van Vleck.[7] The theoretical formula (6) for $M$ has already proved very successful in problems similar to the one under consideration, and one can therefore place considerable reliance upon it. Hence in (8), the only unknown on the right hand side is $x$, and the left hand side is known from experiment.[9] Thus $x$ can be determined. Inserting numerical values, we find

$$374 = 4x - 163 - 51, \quad \text{whence } x = 147 \text{ Cals. .} \qquad . \quad (9)$$

Let us now suppose that an H atom is removed adiabatically from $CH_4$, but that the remaining three H atoms and the C bonds are kept fixed in their tetrahedral positions. The energy of formation of the radical thus obtained will be slightly less than that of ordinary $CH_3$, because, of course, it is not in its most stable position. Thus we can write

$$W(CH_3) - w = 3x - V(v) - 3M(H_2). \qquad . \qquad . \quad (10)$$

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[9] The experimental value for the energy of formation of $CH_4$ depends on the value adopted for the heat of sublimation of carbon, and is subject on this account to an uncertainty of some 10 Cals. Fortunately, our calculations are rather insensitive to such a modification. It becomes increasingly evident that the most fruitful line of research will be to study the variation in any particular bond from compound to compound, rather than the absolute bond energy, since the latter is so difficult to determine experimentally. The very accurate work of Rossini, *Bur. Stan. J. Res.*, 1934, **13**, 21, along these lines is sufficiently accurate to demonstrate conclusively that these variations exist.

Using the above values for $x$, $V(v)$ and $M(H_2)$, we obtain

$$W(CH_3) = 253 + w.$$

The energy required to take an H atom out of methane is therefore $(121 - w)$ Cals. The experimental result [10] that this energy lies between the well-defined limits 98-110 Cals. shows that $w$ is considerably different from zero. Therefore, as an H atom is slowly removed from methane, the $CH_3$ radical remaining gradually changes shape.

## Section 2.

In the present section we endeavour to show that quite general arguments can be advanced to reveal that the most stable configuration of the free methyl radical is a plane one.

Consider for a moment the acetylene molecule. It is known to be linear from the character of its infra-red and Raman spectra. The bonds of the molecule clearly fall into two classes. First there is the linear chain in the line of the molecule, composed of the two $1s$ hydrogen electrons and the $2s$ and $2p\sigma$ electrons of the carbon atoms. Second, there are the $2p\pi$ electrons of the carbon atoms entering into the second and third bonds of the triple bond. Because of the molecular forces, the $2s$ and $2p\sigma$ wave functions will lose their individual significance, and instead one has a pair of hybridised wave functions

$$\psi_1 = \alpha s + \beta p_\sigma, \quad \psi_2 = \beta s - \alpha p_\sigma \qquad . \qquad . \quad (11)$$

with the normalising condition $\alpha^2 + \beta^2 = 1$. A little consideration shows that $\alpha$ and $\beta$ must be nearly equal whatever the relative bonding strengths of the $2s$ and $2p\sigma$ carbon electrons. If, for example, the $2p\sigma$ electrons bind much better than the $2s$, it is possible to construct a very strong C—C bond from the $2p\sigma$ electrons alone, but the C—H bonds thereby suffer considerably and are weak. Similarly, it would be possible to form strong C—H bonds, but then only a feeble C—C bond could be established. The actual situation is then a compromise; approximately one half of the $2p\sigma$ electron on either nucleus is used up in forming a bond with the H atom, and the other half goes into the formation of a bond with the other carbon atom. None of the bonds, therefore, has its best value. If, on the other hand, the $s$-$p$ interplay of (11) is also an extremely important factor in determining the bonding energies, the hybridised wave functions with $2s$ and $2p\sigma$ in about equal proportions should form highly stable bonds.

There is one other case, namely methane, where symmetry arguments fix the hybridisation of $2s$ and $2p\sigma$ wave functions. The wave functions for methane are

$$\psi_t = [s + p_t (3)^{\frac{1}{2}}]/2,$$

where the axis of $p_t$ is along any one of the four tetrahedral directions symbolised by the suffix $t$. Here the mixing is not in equal proportions, but is in the ratio of one $2s$ to three $2p\sigma$.

Although the argument as given here has been presented for simplicity in terms of electron pair bonds, actually it can be developed with similar conclusions for the one electron wave functions of the orbital method. A comparison of the C—H bond in acetylene and in methane should therefore throw valuable light on the relative importance of $2s$ and $2p\sigma$ bonds and of the $2s$-$2p$ interplay.

[10] Bonhoeffer and Harteck, *Grundlagen der Photochemie*, p. 81.

Naturally, it is impossible to make a direct comparison of the energies of the C—H bond in acetylene and methane, but two experimental facts demonstrate pretty conclusively that the bond in acetylene is the stronger. First, the C—H distance in acetylene is smaller than it is in methane. According to Herzberg, Patat and Spinks [11] the C—H distance in acetylene is 1·058 Å.U. The latest and most reliable value for the C—H distance in methane is that of Ginsburg and Barker [12] who give 1·093 Å.U. Second, the C—H force constant [13] is 5·9 × 10$^5$ dynes per cm. in acetylene and only 5·0 × 10$^5$ dynes per cm. in methane. It may be added that the inter-nuclear distance in the CH molecule is 1·12 Å.U. and the force constant as low as 4·5 × 10$^5$ dynes per cm. Here the bonding electron on the carbon nucleus is of the pure $2p\sigma$ type, but comparison with the bonds of methane is not obvious because the C configuration is more like $s^2p^2$ than $sp^3$.

From the above discussion it would appear that pure $2p\sigma$ bonding, although strong, is not quite as firm as that obtained by taking a suitable mixture of $2s$ and $2p\sigma$, the $s$-$p$ interplay more than compensating for the substitution of some $2s$ for $2p\sigma$ in the wave function. In methane, where the ratio of mixing is three $p$ to one $s$, the bonds are probably a little stronger than pure $p$ bonds, and in acetylene, where the mixing of $s$ and $p$ occurs in about equal proportions, the bonds are at approximately their greatest possible strength.

Let us now suppose that we have methyl in the tetrahedral condition in which it exists in methane, and allow it to change slowly to its equilibrium position. From the arguments developed above we see that it will move in the direction where its bonds resemble as closely as possible those of acetylene. The radical will therefore adopt a plane configuration, the bonds of which can be represented :

$$\psi_i = \{(2)^{\frac{1}{2}}\psi_C(2p\sigma_i) + \psi_C(2s)\}/(3)^{\frac{1}{2}},$$

where the axis of $2p\sigma_i$ is along the CH$_i$ line, together with an unsaturated, or free, valency $2p\pi$ perpendicular to the plane of the radical. During the transition, the C—H distances must decrease very slightly and the force constants increase to some extent, due to the increased proportion of $2s$ in the wave function.

## Section 3.

In order to calculate the quantity $w$ of equation (10), we have actually to estimate the change in the energy as CH$_3$ changes from the tetra-hedral to the plane arrangement. We consider separately the variations in $3M(H_2)$, $V(v)$ and $3x$. Assuming for the C—H distance the methane value 1·093 Å.U., it is found from the formula (6) that the term $3M(H_2)$ of (10) gives the plane arrangement 4·2 Cals. greater stability than the tetrahedral, and more stable than any intermediate position. The variations in $V$ and in $3x$ can be estimated from the formulæ of Van Vleck. [7] It appears that $V$ favours the tetrahedral arrangement over all others, but is rather insensitive to changes in the bond angle. Only 3·6 Cals. are needed to rearrange the bonds from the tetrahedral to the plane

[11] Herzberg, Patat and Spinks, *Z. Physik*, 1934, **92**, 87.
[12] Ginsburg and Barker, 1935 New York Meeting, American Physical Society.
[13] Sutherland and Dennison, *Proc. Roy. Soc.*, 1935, **148A**, 250. One must not enquire too closely into what is the exact meaning of these force constants, for in deriving them certain interactions were neglected. These, however, are not such as would invalidate our conclusions.

configuration.   The change in energy as $CH_3$ alters from the tetrahedral to the plane form owing to the variation in $3x$ is given by

$$3\Delta x = 3(N_{ss} - N_{\sigma\sigma})/8 + 0.345\ N_{s\sigma}.$$

Substituting the numerical values of the exchange integrals as given by (7), we find $3\Delta x = 15$ Cals., and it is therefore this term which decides that $CH_3$ must be plane.   Summing up, the value of $w$ is found to be $15.6$ Cals.   Thus according to our theory the energy required to take an H atom adiabatically out of methane is 106 Cals.

It is important to know what is the limit of accuracy in the above theory.   The main error arises from the assumption that the gross energy $x$ of the C—H bond is the same in tetrahedral methyl as in methane. This must be very closely fulfilled, but it is difficult to estimate the error involved.   A variation in $x$ of more than 2 or 3 Cals., however, would be very surprising.   Another possible source of error is that our calculations do not mention explicitly the kinetic energy of the nuclei, or, in other words, the zero point energy.   On this account, the energy $w$ needs alteration by an amount equal to the difference of the zero point energy of plane methyl and three quarters of that of methane.   This quantity must be very small, probably being less than 1 Cal.   The estimate which we have made of the difference of energy of plane and tetrahedral methyl is probably fairly accurate, because we have made it depend to a large extent on the experimental value of a force constant which can be measured accurately.   Thus, on the whole, we are inclined to believe that the estimate of 106 Cals. for the adiabatic heat of the reaction $CH_3 + H \rightarrow CH_4$ has an outside limit of error of $\pm$ 10 Cals., and is probably a good deal better than this.   Experimentally, it is possible only to give upper and lower limits to the heat of the reaction and these are 110 and 98 Cals. respectively.   The agreement is quite satisfactory.   It should be noticed that our calculations apply to an adiabatic change.   Under some experimental conditions it may well happen that as an H atom is torn from methane, the $CH_3$ remaining is left in a state of violent oscillation.   The two reactions

$$CH_4 + Cl_2 \rightarrow CH_3Cl + Cl \quad \text{and} \quad CH_4 + Cl \rightarrow CH_3 + HCl,$$
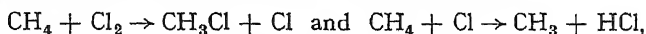
which determine the limits 110 and 98 Cals. respectively, are, however, practically thermo-neutral, and in order that the reactions can occur, all the energy available in $CH_3$ has to be used up, and the radical is left in its ground vibrational state.

### The Substituted Methanes.

A problem closely related to the variation of the stability of the free methyl radical with the H—C—H angle is that of calculating the angles in the various substituted products of methane $CH_3G$, $CH_2G_2$, $CHG_3$.   In a rough calculation we can neglect the various steric repulsions, dipole interactions and Van der Waals attractions between atoms attached to the central carbon atom.   One has then simply C—H and C—G interactions to consider, and one adjusts the angles to get the best possible binding.   Let

$$\psi_H = ap + (1 - a^2)^{\frac{1}{2}}s,$$
$$\psi_G = bp + (1 - b^2)^{\frac{1}{2}}s,$$

be directed wave functions of the C atom, $\psi_H$ being, for example, that of a C electron whose spin is coupled to zero with that of H.   The $p$ wave

functions are directed so that they point to the nucleus indicated by the suffix on $\psi$. Let us conserve the carbon configuration $sp^3$. Then in the case of $CH_3G$ we have $3a^2 + b^2 = 3$, in the case of $CH_2G_2$ we have $2a^2 + 2b^2 = 3$, and in the case of $CHG_3$ we have $a^2 + 3b^2 = 3$. It can easily be shown that the one arbitrary parameter $a$ is determined once the angle between any two bonds is given. Alternatively, if one of these angles is known, $a$ can be calculated. Let us now evaluate the energy of these various compounds by the formula (1), writing it, however, in the slightly different form

$$W = Q - \tfrac{1}{2}\underset{i,k}{\Sigma} J_{ik} + \tfrac{3}{2}\underset{i}{\Sigma} J_{ii},$$

where in the first summation the restriction $i \neq j$ has been removed. The Coulomb energy $Q$ and the first sum of exchange integrals do not depend on the bond angles [14] and can therefore be disregarded. The second sum does involve the bond angles because it depends on $a$ and our problem is to minimise $W$ with respect to $a$ and see how $a$ varies from compound to compound. This is a relatively simple calculation, provided one assumes that the departures from the tetrahedral angle are small. Writing

$$a^2 = q + \tfrac{3}{4}, \qquad . \qquad . \qquad . \qquad . \quad (12)$$

so that $q$ is a measure of the deviation from the tetrahedral $109 \cdot 5°$, it is found that the energies of the various substituted products of methane all have the form

$$W = Const. - Aq + Bq^2 + \ldots$$

The value of $q$ giving a minimum $W$ is therefore

$$q = A/2B. \qquad . \qquad . \qquad . \qquad . \quad (13)$$

Using the suffix 1 to refer to $CHG_3$, 2 to refer to $CH_2G_2$ and 3 to refer to $CH_3G$, we find

$$\left.\begin{array}{l} A_1 = 3[N_{\sigma\sigma} - N_{ss} - \mathbf{N}_{\sigma\sigma} + \mathbf{N}_{ss} - 2(N_{s\sigma} - \mathbf{N}_{s\sigma})/(3)^{\frac{1}{2}}]/2, \\ A_2 = 2A_1, \quad A_3 = 3A_1, \\ B_1 = 8(N_{s\sigma} + \mathbf{N}_{s\sigma}/3)/(3)^{\frac{1}{2}}, \\ B_2 = 16(N_{s\sigma} + \mathbf{N}_{s\sigma})/(3)^{\frac{1}{2}}, \\ B_3 = 24(N_{s\sigma} + 3\mathbf{N}_{s\sigma})/(3)^{\frac{1}{2}}, \end{array}\right\} \quad (14)$$

where the $N$ are carbon-hydrogen and the $\mathbf{N}$ are carbon-$\mathbf{G}$ diatomic exchange integrals defined by

$$N_{\alpha\beta} = - \int\psi_H(1s_1)\psi_C(\alpha_2)H\psi_H(1s_2)\psi_C(\beta_1)dv_1 dv_2,$$
$$\mathbf{N}_{\alpha\beta} = - \int\psi_G(2p\sigma_1)\psi_C(\alpha_2)H\psi_G(2p\sigma_2)\psi_C(\beta_1)dv_1 dv_2.$$

As a consequence of the above we have

$$q_1 : q_2 : q_3 = 1/1 + \theta/3 : 1/1 + \theta : 1/1 + 3\theta, \quad . \qquad . \quad (15)$$

where $\theta = \mathbf{N}_{s\sigma}/N_{s\sigma}$. Thus if $\theta$ is known the relative values of $q_1$, $q_2$ and $q_3$ are determined. Now $\theta$ cannot differ much from unity and therefore, roughly at any rate,

$$q_1 : q_2 : q_3 = 3 : 2 : 1.$$

In order to calculate the $q$'s from the experimental data one proceeds [7] as follows. Let $(180 - 2\omega)$ be the H—C—G angle in $CH_2G_2$. Then $a_2{}^2 = (3 - \sec^2 \omega)/2$. Let $\theta$ denote the angle between the C—G axis

[14] W. G. Penney, *Proc. Roy. Soc.*, 1934, **146A**, 228.

and a C—H axis in $CH_3G$.  Then $a_3{}^2 = (2 \cosec^2 \theta)/3$.  Similarly, if $\phi$ is the angle between the C—H axis and a C—G axis in $CHG_3$, then $a_1{}^2 = (1 - 2 \cot^2 \phi)$.  Once $a$ is known, the value of $q$ follows immediately from (6).

Let us apply the relations (12), (13) and (14) to discover, for example, how the valency angles in $CH_3$—$CH_3$ (ethane), differ from those in methane.  We have first to calculate $q = A_3/2B_3$ from the C—H and C—C exchange integrals.  Now the exact magnitudes of these are not known and therefore we cannot give an exact answer to our problem.  However, it is easy to see from the form of $A_3$ and $B_3$ that $q$ must be very small. Thus $B_3$ is built up of two terms, both of the same sign.  The two integrals $N_{s\sigma}$ and $N_{s\sigma}$ are positive and both are approximately of magnitude 2 e.v.  Hence $B_3$ can hardly be less than 100 e.v.  In contrast with this, $A_3$ is built up of small differences of varying sign ; as a result it can hardly exceed 2 or 3 e.v.  The order of magnitude of $q$ is seen to be 0·01 and is certainly less than 0·02.  The corresponding variations of the valency angles from the tetrahedral value are 1° and 2° respectively. When a second and then a third H atom are replaced by methyl groups, the departures of the C—C—C angles from the tetrahedral value are 2°, (4°), and 1° (2°), respectively, the values in brackets being the upper limits corresponding with the upper limit 2° for $CH_3$—$CH_3$.

Another example on which the theory may be tested is the chloro-methanes.  Here, however, direct application of the theory is open to question because of the neglect of polar terms.  We know that, in so far as the situation is governed chiefly by the non-polar [15] terms, only small deviations from the tetrahedral angle can occur.  Let us consider for a moment the polar terms in $CH_3Cl$, and try to discover how the shape of the molecule is modified by them.  Their principal influence on the shape is of an indirect nature.  Thus, for example, the polar terms give a partial migration of charge towards the chlorine nucleus.  As a result the H—H repulsions are increased, while the H—Cl repulsions are diminished. The influence of the polar terms thus tends to increase the HCH angle from 110 to 120°.  The non-polar terms, however, resist very strongly any departure from the tetrahedral angle ; since the complete wave function of $CH_3Cl$, in order to fit the observed dipole moment, must be on the average five-sixths non-polar and one-sixth polar, we do not expect the polar terms to cause a deviation of more than a degree or two from the tetrahedral angle.  A compound where the polar terms are particularly large, and may therefore be expected to have an appreciable effect, is $CH_3F$, and it should be possible in this case to detect the opening out of the HCH angle.

A criticism of the theory which we have developed is that it takes no account of steric repulsions or Van der Waals attractions between the groups attached to the central carbon atom.  Let us again consider the chloro-methanes.  The Cl atoms are large and consequently the C—Cl distance ($1·76 \times 10^{-8}$ cm.),[16] is considerably greater than the C—H distance ($1·09 \times 10^{-8}$ cm.).[12]  Because of this, the interaction of any two Cl atoms, or of a Cl and an H atom, may be little greater than that

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[15] It will be noticed that we say nothing about the ionic terms.  These are of an instantaneous polar nature, but give no dipole moment in a time average. There seems to be no method of evaluating the effect of the ionic terms on the bond angles, but clearly from their very nature they select a configuration which is exactly, or is very close to, the symmetrical tetrahedral position.

[16] Pauling and Brockway, *J. Chem. Physics*, 1934, **2**, 867.

between two H atoms. In fact, assuming that two Cl atoms repel each other like two Ar atoms, it is possible to make an estimate of their interaction from a formula given by Lennard-Jones.[17] Thus, if the tetrahedral angles are conserved in $CH_2Cl_2$, the Cl—Cl steric repulsion is 8 Cals. compared with the H—H steric repulsion of 8·5 Cals. The Cl—Cl Van der Waals attraction is 3·5 Cals., and this probably exceeds the Van der Waals attraction between the hydrogen atoms. Unfortunately, it does not seem possible to make any estimate of the H—Cl interaction, but something of the same order of magnitude may be confidently anticipated. In general, one would not expect the sum of the steric repulsions and Van der Waals attractions to have a minimum when the angles of the molecule were exactly tetrahedral, although the minimum must occur fairly close to this. The force constant, arising from the directed valencies, for small variations in the bond angles is so large that the influence of the steric repulsions to shift the angles of the molecule from those required by the directed valencies, must be quite small and of the order of a degree or two.

While our theory does not, therefore, give any exact information on the variation of the valency angles of the substituted methanes from the tetrahedral value, it does show that the departures are remarkably small and are of the order of two or three degrees. The latest experimental evidence from two independent sources is in excellent accord with this conclusion. From a mathematical analysis of the infra-red vibration spectra of the methyl halides Dennison and Johnston [18] find for the moment of inertia C about the axis of symmetry, the values 5·62, 5·48, 5·45 and 5·45 × $10^{-40}$ respectively, for $CH_3F$, $CH_3Cl$, $CH_3Br$ and $CH_3I$. The corresponding moment of inertia for $CH_4$ is 5·47 × $10^{-40}$. Only in the case of $CH_3F$ is there any real variation from the tetrahedral angle, and even here the deviation is surprisingly small. From electron diffraction measurements Brockway and Sutton [19] find that the Cl—C—Cl angles in $CH_2Cl_2$ and $CHCl_3$ are inappreciably different from tetrahedral, although the method is hardly accurate enough to reveal variations of the order of a degree or two.

## Summary.

The variation of the energy of a polyatomic molecule with the bond angles as given by the formula of localised pairs, can be used to calculate some of the vibration frequencies of the molecule. Alternatively, it is possible to determine the exchange integrals from the observed values of the frequencies. The substitution of the values found in this way, into the formula of perfect pairing, should give quite accurately the variation of the

[17] Lennard-Jones, *Proc. Physic. Soc.*, 1931, **43**, 475.

[18] Dennison and Johnston, *Physic. Rev.*, 1935, **47**, 93. Professor Dennison has called the author's attention to the fact that there is a numerical error in this letter. For the $ZYX_3$ molecule, the sum of the spacings of the perpendicular bands is

$$\Delta \nu = h\{3/C - 7/2A\}/4\pi^2.$$

The incorrect formula given in the letter is the same as that above, except that it has 5 instead of 7. The corrected values of C for $CH_3F$, $CH_3Cl$, $CH_3Br$ and $CH_3I$ are 5·62, 5·48, 5·45 and 5·45 × $10^{-40}$ respectively. By a similar calculation, C for methane is 5·47. The discrepancy between this value and the value 5·298, obtained by Barker and Ginsburg by direct experiment on the parallel bands of $CH_3D$, shows that the anharmonic terms are not negligible.

[19] The author wishes to thank Drs. Brockway and Sutton for this information in advance of publication.

energy with bond angle. As an example, the frequency $\nu_2$ of the methane molecule is used to determine some fundamental C—H exchange integrals. These are then employed to demonstrate that the most stable form of the $CH_3$ radical has a plane configuration. The heat of the reaction

$$H + CH_3 \rightarrow CH_4$$

is calculated to be about 106 Cals., in satisfactory agreement with experiment. A rough calculation, along similar lines, is made of the valency angles in the substituted methanes. It is shown that if some or all of the H atoms in $CH_4$ are replaced by other mono-valent groups, the resulting deviations from the tetrahedral angle are remarkably small, and can hardly exceed a few degrees.

In conclusion I should like to express my thanks to Professor J. E. Lennard-Jones and to Dr. G. Sutherland for helpful discussions.

# A NOTE ON THE SPECIFIC HEAT OF A LIQUID AND ITS VAPOUR AND ITS APPLICATION TO THE HEAT OF REACTION IN LIQUID MIXTURES.

By D. B. MACLEOD, M.A., D.Sc.

(*Communicated by Eric K. Rideal, F.R.S.*)

Our knowledge of the specific heat of liquids is, admittedly, unsatisfactory. It is not difficult to show that the work done in overcoming the internal forces of a liquid is not greater than about 1 per cent. of the total work done in raising the liquid 1 degree. The specific heat of liquids is definitely greater than that of their vapours at the same temperature and this difference is much greater than can be explained by the work done to expand the liquid against the internal forces. The difference, therefore, must be largely due to the greater number of degrees of freedom in the liquid condition. The author is not aware that attention has been drawn to the matter, but it became noticeable on a study of the data available, that there is an almost constant difference between the gram molecular heats of liquids at ordinary temperatures and their vapours at the same temperature. Further, this difference is very close to 9 cals. This is borne out by reference to Table I. The data are mostly obtained from the tables of Lanbolt-Börnstein, 1923. In some cases it is unsatisfactory, as it is not possible to obtain the values for the liquid and the vapour at exactly the same temperature. In the case of the liquids, the values are at constant pressure, which would be about 1 per cent. higher than at constant volume.

The values for the vapours are at constant volume, calculated in most cases from the values at constant pressure and the known ratio of the two specific heats. $C_1$ is the specific heat per gram and $C_2$ per gram molecule. The last column gives the difference between the molecular heats of the liquid and its vapour.

The figures for ethyl chloride are valuable. The specific heats were

TABLE I.

| Substance. | Liquid. | | | Vapour. | | | Diff. |
|---|---|---|---|---|---|---|---|
| | Temp. °C. | $C_1$. | $C_2$. | Temp. °C. | $C_1$. | $C_2$. | |
| Chlorine . . . | 30 | ·240 | 18·3 | 17 | ·13 | 8·5 | 9·8 |
| Bromine . . . | 13-45 | ·107 | 17·1 | 83-228 | ·043 | 6·8 | 10·3 |
| Ammonia . . | 0-26 | 1·08 | 18·3 | 18 | ·40 | 6·8 | 11·5 |
| Carbon disulphide . | 30 | ·240 | 18·3 | 17 | ·13 | 10·0 | 8·3 |
| Acetone . . . | 20 | ·514 | 29·8 | 26-110 | ·33 | 19·9 | 9·9 |
| Ethyl acetate . | 20 | ·478 | 42·1 | 35-189 | ·34 | 30·0 | 12·1 |
| Ethylene chloride . | 30 | ·305 | 30·2 | 111-221 | ·21 | 21·0 | 9·2 |
| Ethyl bromide . . | 5-10 | ·216 | 23·6 | 28-116 | ·13 | 14·1 | 9·5 |
| Benzene . . . | 20 | ·410 | 32·0 | 20 | ·27 | 21·0 | 11·0 |
| Chloroform . . | 20 | ·234 | 27·9 | 28-189 | ·18 | 17·0 | 10·9 |
| Carbon tetrachloride | 0 | ·201 | 30·9 | 0 | ·13 | 20·0 | 10·9 |
| Ether . . . | 10 | ·54 | 40·0 | 16 | ·42 | 31·0 | 9·0 |
| Water . . . | 100 | 1·00 | 18·0 | 100 | ·36 | 6·5 | 11·5 |
| Ethyl chloride . . | −30 | ·348 | 23·4 | −30 | ·20 | 12·9 | 10·5 |
| | 40 | ·413 | 26·5 | 40 | ·26 | 16·7 | 9·8 |

determined by Jenkin.[1] The increase of the specific heat for both the liquid and the vapour from − 30° C. to + 40° C. is practically the same, namely 0·065 for the liquid and ·06 for the vapour. The difference per gram molecule is about 10 cals.

As one degree of freedom corresponds to a specific heat of 1 calorie per gram molecule, these figures mean that a liquid has nine to ten more degrees of freedom than its vapour at the same temperature.

It is not difficult to account for three degrees of freedom with certainty. Mercury has an atomic heat in the liquid form of practically six, indicating that it has both kinetic and potential energy, each having three degrees of freedom, whereas a monatomic gas has an atomic heat of only 3. Andrade[2] draws attention to the fact that the molecules of a liquid can be considered to oscillate in a manner similar to those in a solid. We should expect a liquid, therefore, to gain three degrees of freedom in this way over and above the number, due to atomic vibrations within the molecule, which it has in common with its vapour. They may both be assumed to have the same energy in the form of rotation. There remain, therefore, a further six degrees to be accounted for.

There are two essential differences between molecular collisions in the liquid and vapour conditions. In the vapour the collision frequency is very low, of the order of $10^8$ or $10^9$ times per sec.,whereas in the liquid condition, as pointed out by Andrade,[2] it is of the order of $10^{12}$ to $10^{13}$ times per sec. Further, in the vapour, the molecule is free to move off in any direction on the approach of a colliding molecule, whereas in a liquid it is held in constraint by the neighbouring molecules during a collision. In the latter case, therefore, the molecule or the molecular field might be expected to undergo a distortional vibration, of the order of frequency of the fundamental vibration of the molecule, which would be largely absent in the vapour form. As this distortional vibration would be of a low order of frequency it would not be affected by quantum considerations but would give rise to six degrees of freedom,

[1] *Trans. Faraday Soc.*, 1922, 197.
[2] " Theory of the Viscosity of Liquids," *Phil. Mag.*, 1934, 17, 497.

three of kinetic and three of potential energy. The energy would be equivalent to energy of strain of the molecular fields. A simple mono-atomic atom such as mercury would not be expected to show these vibrations, accounting for the fact that mercury gains only three degrees of freedom whereas the more complex molecules gain nine degrees.

Apart, then, from the energy of vibration of the atoms within the molecule, which a liquid at any given temperature might be expected to share in common with its vapour at the same temperature, a liquid molecule might be expected to have fifteen degrees of freedom made up as follows : six degrees of kinetic and potential energy due to translation, three degrees of rotation, and six degrees of distortional.

Many pairs of liquids, on mixing, evolve considerable amounts of heat. There is very substantial evidence that, though the nature of the combination is somewhat ill defined, definite compounds are formed in these cases. Many of these compounds consist of one molecule of one liquid combining with one molecule of the other. It is noticeable in these reactions [3]—when allowance has been made for the amount of combination taking place—that the heat of reaction is very similar and of the order of 5000-6000 cals. per gram molecule. It becomes of interest, therefore, to analyse the possible sources of this heat of reaction.

If two molecules combine to form a single molecule, it is certain that if the compound has any rigidity at all, there will be a loss of degrees of freedom. At ordinary temperatures, say 300° K., the loss of one degree of freedom would liberate 300 cals. per gram molecule as heat of reaction. It has been pointed out that a liquid molecule may have as many as fifteen degrees of freedom, apart from the degrees of freedom of the atoms within the molecule. How many of these degrees of freedom might two molecules combining to form a single molecule, be expected to lose ? If the combination has any reality at all, the energy of translation and rotation would be halved, liberating nine degrees of freedom, or 2700 cals. per gram molecule of the compound formed, at 300° K. It is more open to doubt whether the remaining six degrees would halve, making the heat liberated equal to 4500 cals. This amount of heat would be common to reactions of this type and the difference between this amount and the actual amount would be accounted for by the change of potential energy between the reacting molecules due to the combination. As has been pointed out, the combination in this type of reaction is generally due to the stray valencies of the molecule and is only appreciable in the liquid condition where the continued close proximity of the molecules favours some form of association. The actual energy of combination would, therefore, be small and not very different with different pairs of liquids. If the above analysis is correct, the heat of reaction should increase with the absolute temperature at which the combination takes place. At present, on account of the difficulty of estimating quantitatively the amount of combination taking place and the lack of data on the heats of reaction at various temperatures, it is not possible to check the truth of this statement.

I wish to thank Dr. C. Coleridge Farr, F.R.S., for his continued interest and criticism.

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       *New Zealand.*

    [3] *Cf.* Bramley, *J.C.S.*, 1916, **109**, 434-519, o-chlorophenol and quinoline, o-chlorophenol and pyridine, o-chlorophenol and acetone, chloroform and ether.

# PROPERTIES OF ELECTROLYTIC SOLUTIONS. XVI. CONDUCTANCE OF ELECTROLYTES IN ANISOLE, ETHYLENE BROMIDE, AND ETHYLENE CHLORIDE AT 25°.

By Norman L. Cox,[1] Charles A. Kraus, and Raymond M. Fuoss.

In earlier papers of this series, Fuoss and Kraus[2] have shown that the conductance of electrolytic solutions as a function of concentration may be accounted for quite generally by combining mass action effects, due to short range interaction of ions, with ion-atmosphere effects, due to long range interaction. In solvents of very low dielectric constant $(< 10)$, it is necessary to take into account the equilibrium between ions, ion pairs and triple ions as well as that between simple ions and ion pairs. It was the purpose of the present investigation to subject the theory to a more rigid test. To accomplish this, it was necessary to develop the technique of conductance measurements in several respects in order that reliable data might be obtained over a wide concentration range and at concentrations approaching $10^{-6}N$.

In carrying out measurements at low concentrations, the two major experimental difficulties are : (1) lack of suitable resistances of the order of several megohms and (2) the appearance of sorption effects at concentrations below $10^{-5}N$. Errors due to sorption are accentuated in solvents of low dielectric constant owing to the fact that, in order to keep the resistances reasonably low, it is necessary to employ large electrode surfaces.

Solvents, in the dielectric constant range 4 to 10, were chosen with a view to their stability and ease of purification and manipulation. The solvents employed were anisole $(D = 4.29)$, ethylene bromide $(D = 4.76)$ and ethylene chloride $(D = 10.23)$. In the last-named solvent, the value of $\Lambda_0$ can be satisfactorily evaluated from data between $10^{-4}$ and $10^{-6}N$. Tetra-*n*-butylammonium and tetra*iso*amylammonium salts were employed as solutes.

## Experimental.

**Apparatus.**—The usual alternating current method of measuring resistance was employed. The measuring unit consisted of a Jones bridge,[3] a vacuum tube oscillator, having a frequency range from 400 to 4000 cycles/sec., an amplifier and a telephone. The measuring apparatus was housed in a sound-proof room, the walls of which were grounded,

and due precautions were taken in the insulation and screening of the lead wires.

Capacity and induction-free resistances of the usual type were available up to 200,000 ohms. After testing various commercial types of high resistances, it was found that wire-wound resistances manufactured by the Shallcross Manufacturing Company of Collingdale, Pennsylvania, could be satisfactorily employed up to 3 megohms. It is important to point out, however, that only two such coils could be used in circuit at one time and then only when separated at some distance. The resistances gave readings independent of frequency up to 3 megohms. The coils were checked at frequent intervals against standard resistances and were found to be remarkably constant.

Four cells were used whose constants were determined by comparison with a fifth cell which, in turn, was compared with a cell standardised with 0·1 demal potassium chloride, using the value of Parker.[4] The constants of the four cells were as follows : Cell 1, 0·017370 ; Cell 2, 0·06226 ; Cell 3, 0·003048 ; Cell 4, 0·0011043. Cells 1 and 2 were constructed with plate electrodes and Cells 3 and 4 with three concentric, cylindrical electrodes. In the case of Cell 4, the three cylinders had diameters of 17, 19, and 21 mm., a length of 80 mm. and a total surface of approximately 300 cm.[2]. The cells were constructed of Pyrex glass. Reliable seals cannot be made by means of platinum tubing sealed directly through Pyrex glass but the difficulty may readily be overcome by overlaying pure platinum tubing (diameter, 1·2 mm., thickness, 0·05 mm.) with Corning glass No. 707, which successfully seals into Canary glass (Corning glass No. 332) which, in turn, is readily sealed to Pyrex glass.[5] Electrodes were not platinised. For intercomparing the cells, solutions of tetrabutylammonium nitrate in anisole proved convenient and satisfactory. The cells were designed to minimise capacity effects due to leads and were provided with interchangeable ground glass caps for closing and for introducing and withdrawing solvent or solution.

Temperatures were controlled by means of an oil-filled thermostat at 25 ± 0·002°.

Concentrations were determined by weight and both the concentration and the dilution methods were employed in the measurements. Excepting when sorption effects appeared, the two methods yielded identical results within the limit of experimental error.

Materials.—Anisole was purified according to the method of Bien, Kraus and Fuoss.[6] Ethylene bromide, after distillation and discarding of higher and lower fractions, was washed with concentrated sulphuric acid, dilute sodium hydroxide, and water. After drying with calcium chloride, it was fractionally crystallised several times and then treated with activated aluminium oxide. This oxide is one of the most convenient and successful agents for final purification of solvents ; it invariably lowers the conductance of solvents far below values obtained by other methods. The ethylene bromide was transferred from the storage vessel over aluminium oxide through a glass filter to the conductance cell, the filter serving the purpose of removing particles of oxide. Ethylene bromide cannot be purified for conductance purposes by distillation.

Ethylene chloride, after initial distillation and rejection of higher and lower fractions, was treated like ethylene bromide, except that the solvent was transferred from the storage vessel to the cells by distillation from aluminium oxide. The best figures for solvent conductance were as follows : ethylene chloride, $5 \times 10^{-12}$ mho ; ethylene bromide, $8 \times 10^{-13}$ mho ; anisole, $3 \times 10^{-14}$ mho. In practice, the solvents usually had somewhat higher conductances but seldom ten times the values here given.

[4] Parker and Parker, *J. Amer. Chem. Soc.*, 1924, **46**, 312.

[5] The details of constructing these seals were worked out by Mr. Vincent F. Hnizda of this laboratory.

[6] Bien, Kraus and Fuoss, *J. Amer. Chem. Soc.*, 1934, **56**, 1860.

In no case was the conductance of the solvent greater than $0 \cdot 1$ per cent. of that of the solution measured.

The salts employed were : tetra-$n$-butylammonium-nitrate, thiocyanate, bromide, picrate, and acetate, and tetra$iso$amylammonium nitrate. The preparation of tetra$iso$amylammonium salts has been described by Fuoss and Kraus.[2] The tetra-$n$-butylammonium salts were prepared in a similar manner although, it may be noted, the reaction between tributylamine and butyliodide proceeds much more readily than the corresponding reaction in the case of the amyl derivative. Samples of tetrabutylammonium iodide, which served as source material, were analysed for iodine ; found 34·20, 34·16, 34·35 per cent. ; calculated, 34·38 per cent. The bromide, acetate and picrate were prepared by adding the corresponding acids, in slight excess, to solutions of the base (prepared from pure iodide) in water or in alcohol. Tetrabutylammonium nitrate was prepared by metathesis of the iodide with silver nitrate in alcohol and tetrabutylammonium thiocyanate by metathesis of the nitrate with potassium thiocyanate in absolute alcohol. Tetrabutylammonium iodide was recrystallised from anhydrous ethyl acetate (M.P. 144°) ; tetrabutylammonium nitrate was recrystallised from benzene (M.P. 120°). This salt crystallises from alcohol in a metastable form which is highly soluble in benzene ; crystallisation from benzene may be induced by scratching the surface of the containing vessel or by seeding with a crystal of the stable form. The crystals contain benzene. Tetrabutylammonium bromide was recrystallised from anhydrous ethyl acetate (M.P. 113°). Tetrabutylammonium picrate was recrystallised from ethylene chloride and petroleum ether (M.P. 89°). Tetrabutylammonium acetate was recrystallised from benzene with addition of petroleum ether (M.P. 116°) and tetrabutylammonium thiocyanate was recrystallised from a mixture of benzene and ether (M.P. 123°).

**Sorption Effects.**—Sorption effects make their appearance in the neighbourhood of $10^{-5}N$. The effects are greater in anisole than in ethylene chloride and greater for nitrates and similar salts than for picrates. Adsorption was particularly marked in the case of the acetate. On introducing 100 c.c. of a $0·82 \times 10^{-6}N$ solution of tetrabutylammonium nitrate in anisole into Cell 4, the initial resistance was 2·2 megohms and increased to 6·0 megohms in the course of an hour ; on mixing the contents of the cell, the conductance returned to 2·3 megohms. After five days, the resistance reached a value of 16 megohms for the completely mixed solution. Desorption effects are less marked than adsorption effects, for which reason measurements in anisole at lower concentrations were carried out by the dilution method in the case of all salts, excepting the picrate. On diluting a solution of tetrabutylammonium nitrate in anisole from $5·8 \times 10^{-6}N$ to $1·2 \times 10^{-6}N$, the conductance was 7 per cent. high ; on making up a fresh solution (230 c.c.) in a clean flask at the same concentration and introducing this into the cell, the conductance was 13 per cent. low. In the first case, the high value of the conductance was due to desorption from the electrodes, in the second, to adsorption of the electrolyte on the walls of the flask in which the solution was prepared. With tetrabutylammonium nitrate in anisole, errors due to desorption became small at $10^{-5}N$.

To obtain satisfactory conductance values when sorption occurs, it is necessary to prepare repeatedly solutions of a given concentration in the same vessel and to introduce these successively into the cell to replace preceding solutions. With a solution of tetrabutylammonium nitrate in anisole at $1·009 \times 10^{-6}N$, which had been diluted from a concentration of $2·064 \times 10^{-6}N$, the initial equivalent conductance (based on the concentration given) was 0·4945. After preparing a fresh stock solution in a flask and introducing the same into the cell, the conductance fell to 0·4706 and, on again repeating the process, it fell to 0·4567. The introduction of a quantity of clean, glass beads into this solution reduced its

conductance 40 per cent. Tetrabytylammonium picrate exhibits only slight desorption effects ; the conductance value obtained in one series of dilutions was only 2·2 per cent. high at approximately $10^{-6}N$.

In ethylene chloride, sorption effects are much less marked than in anisole and measurements above $10^{-5}N$ could be carried out by the concentration method (except in the case of the acetate). At lower concentrations, it was necessary to replace the solutions several times before a constant value of conductance was reached. This is illustrated in the following table where values of $\Lambda$ are given for successive solutions of tetrabutylammonium nitrate of the same initial concentration. The equivalent conductances given are slightly in error, excepting the last one in each series, since the observed specific conductances were

TABLE I.—INFLUENCE OF ADSORPTION ON CONDUCTANCE IN ETHYLENE CHLORIDE.

| $C \times 10^6$. | $\Lambda_1$. | $\Lambda_2$. | $\Lambda_3$. | $\Lambda_4$. |
|---|---|---|---|---|
| 1·548 | 57·49 | 63·07 | 63·60 | 63·69 |
| 2·982 | 61·70 | 62·70 | 62·60 | — |
| 5·812 | 60·50 | 61·19 | — | — |
| 10·95 | 58·64 | 59·13 | — | — |

divided by the concentration of the solution as added.

When a series of measurements is carried out by the concentration method, the equivalent conductance, calculated without allowing for adsorption effects, passes through a maximum as was also observed by Fuoss [7] at an earlier date. In the following table are given data for a series of measurements with tetrabutylammonium nitrate in ethylene chloride in which known quantities of electrolyte were successively added to a known quantity of solvent. The concentrations are given in the first column, the equivalent conductances (calculated from the observed specific conductance of the solutions) in the second column, and the true equivalent conductances in the third column.

TABLE II.—ADSORPTION IN ETHYLENE CHLORIDE.

| $C_{exp.} \times 10^6$. | $\Lambda_{exp}$. | $\Lambda_{calc}$. | $10^7 \, l_{exp}$. | $C_{calc.} \times 10^6$. | $\Delta C \times 10^6$. |
|---|---|---|---|---|---|
| 2·87 | 52·6 | 63·0 | 1·51 | 2·40 | 0·47 |
| 4·56 | 54·3 | 62·0 | 2·47 | 3·98 | 0·58 |
| 6·58 | 54·4 | 60·5 | 3·82 | 6·33 | 0·55 |
| 9·36 | 55·7 | 59·5 | 5·21 | 8·77 | 0·59 |
| 12·17 | 55·5 | 58·3 | 6·76 | 11·61 | 0·56 |
| 18·51 | 54·5 | 56·0 | 10·09 | 18·02 | 0·49 |

As may be seen from the table, the equivalent conductance passes through a maximum at about $10^{-5}N$. On dividing the observed specific conductance (col. 4) by the true equivalent conductance as determined from other measurements (col. 3), the true concentrations of the solutions are obtained as given in column 5. The differences between the original concentrations and the concentrations of column 5 represent the adsorbed electrolyte, given in the last column. It will be noted that these values are constant within the limit of experimental error. The total volume of solution was 100 c.c. and the concentration change in the last column corresponds to an adsorption of $5·4 \times 10^{-8}$ moles. Since the total area of the electrodes was 20 cm.², this indicates an adsorbed layer of monomolecular thickness.

[7] Fuoss, *unpublished observations.*

The results presented above make it clear that accurate conductance measurements below $10^{-5}N$ cannot be obtained unless appropriate means are adopted to eliminate the effects due to adsorption.  In the measurements for which data are recorded below, necessary precautions were taken.

## Results.

The experimental results are presented in Tables III.-V., which require little explanation.  From two to six independent series of measurements

TABLE III.—CONDUCTANCE VALUES IN ANISOLE.

| $C \times 10^4$. | $\Lambda \times 10^2$. | $C \times 10^4$. | $\Lambda \times 10^2$. | $C \times 10^4$. | $\Lambda \times 10^2$. |
|---|---|---|---|---|---|

### A. Tetra-$n$-butylammonium Nitrate.

| | | | | | |
|---|---|---|---|---|---|
| 2·190 | 4·122 | 0·7799 | 5·802 | 0·1441 | 12·45 |
| 1·056 | 5·220 | ·5628 | 6·700 | ·05802 | 19·70 |
| ·9236 | 5·530 | ·3365 | 9·964 | ·02064 | 32·50 |
| ·8199 | 5·700 | ·1923 | 10·84 | ·01009 | 47·13 |

### B. Tetra-$n$-butylammonium Bromide.

| | | | | | |
|---|---|---|---|---|---|
| 151·3 | 8·050 | 15·45 | 2·929 | 1·970 | 3·197 |
| 95·09 | 6·029 | 9·872 | 2·756 | 1·852 | 3·210 |
| 56·53 | 4·560 | 6·229 | 2·721 | 0·9295 | 3·952 |
| 54·49 | 4·492 | 3·757 | 2·813 | ·8020 | 4·241 |
| 32·62 | 3·616 | 3·454 | 2·849 | ·3614 | 5·935 |
| 28·99 | 3·463 | 2·869 | 2·935 | ·1426 | 9·193 |

### C. Tetra-$n$-butylammonium Thiocyanate.

| | | | | | |
|---|---|---|---|---|---|
| 106·5 | 8·343 | 14·01 | 4·060 | 2·066 | 5·339 |
| 90·78 | 7·596 | 9·499 | 4·003 | 1·459 | 6·027 |
| 66·42 | 6·448 | 9·152 | 4·016 | 1·072 | 6·686 |
| 61·75 | 6·207 | 8·507 | 4·048 | 0·7287 | 8·031 |
| 41·11 | 5·218 | 5·492 | 4·205 | ·5660 | 8·664 |
| 40·36 | 5·181 | 5·045 | 4·282 | ·5454 | 8·929 |
| 28·85 | 4·641 | 4·570 | 4·333 | ·3186 | 11·58 |
| 24·36 | 4·442 | 2·885 | 4·641 | ·1856 | 15·18 |
| 16·14 | 4·072 | 2·197 | 5·202 | — | — |

TABLE III.—D. Tetra-$n$-butylammonium Picrate.

| Series, No. | $C \times 10^4$. | $\Lambda_{obs.} \times 10^2$. | $\Lambda_{calc.} \times 10^2$. | $(\Lambda_o - \Lambda_c) \times 10^2$. | Per Cent. |
|---|---|---|---|---|---|
| I, 1 | 166·2 | 11·24 | — | — | — |
| 2 | 101·6 | 7·593 | — | — | — |
| 3 | 60·48 | 5·876 | — | — | — |
| 4 | 35·02 | 5·239 | — | — | — |
| II, 1 | 8·425 | 6·440 | 6·439 | +0·001 | +0·01 |
| 2 | 4·252 | 8·248 | 8·252 | −0·004 | −0·05 |
| 3 | 2·221 | 10·86 | 10·849 | +0·011 | +0·10 |
| 4 | 1·048 | 15·28 | 15·276 | +0·004 | +0·03 |
| 5 | 0·5165 | 21·33 | 21·354 | −0·024 | −0·11 |
| 6 | ·2752 | 28·95 | 28·953 | −0·003 | −0·01 |
| III, 1 | 1·659 | 12·31 | 12·357 | −0·047 | −0·40 |
| 2 | 0·6856 | 18·64 | 18·654 | −0·014 | −0·08 |
| 3 | ·2838 | 28·53 | 28·53 | 0·0 | ±0·00 |
| 4 | ·09798 | 48·14 | 48·03 | +0·11 | +0·22 |
| 5 | ·03551 | 79·61 | 79·26 | +0·35 | +0·44 |
| 6 | ·01346 | 131·1 | 128·2 | +2·90 | +2·21 |

TABLE IV.—CONDUCTANCE VALUES IN ETHYLENE BROMIDE.

| $C \times 10^4$. | $\varLambda \times 10^2$. | $C \times 10^4$. | $\varLambda \times 10^2$. | $C \times 10^4$. | $\varLambda \times 10^2$. |
|---|---|---|---|---|---|

### Tetra-$n$-butylammonium Nitrate.

| $C \times 10^4$. | $\varLambda \times 10^2$. | $C \times 10^4$. | $\varLambda \times 10^2$. | $C \times 10^4$. | $\varLambda \times 10^2$. |
|---|---|---|---|---|---|
| 110·7 | 10·72 | 6·712 | 11·06 | 0·3301 | 39·99 |
| 56·14 | 8·418 | 3·082 | 14·75 | ·1193 | 66·43 |
| 36·89 | 8·034 | 1·282 | 21·55 | ·06808 | 90·40 |
| 28·27 | 8·015 | 0·7441 | 26·88 | ·04440 | 108·6 |
| 22·67 | 8·103 | ·4885 | 33·26 | — | |

TABLE V.—CONDUCTANCE VALUES IN ETHYLENE CHLORIDE.

| $C \times 10^4$. | $\varLambda$. | $C \times 10^4$. | $\varLambda$. | $C \times 10^4$. | $\varLambda$. |
|---|---|---|---|---|---|

### A. Tetra-$n$-butylammonium Picrate.[8]

| $C \times 10^4$. | $\varLambda$. | $C \times 10^4$. | $\varLambda$. | $C \times 10^4$. | $\varLambda$. |
|---|---|---|---|---|---|
| 14·90 | 23·45 | 2·072 | 37·82 | 0·4488 | 47·82 |
| 8·229 | 27·42 | 1·307 | 41·21 | ·2971 | 49·78 |
| 4·243 | 32·31 | 0·9402 | 43·41 | ·1792 | 51·56 |
| 2·112 | 37·25 | ·7444 | 44·96 | ·1041 | 52·86 |

### B. Tetra-$n$-butylammonium Acetate.

| $C \times 10^4$. | $\varLambda$. | $C \times 10^4$. | $\varLambda$. | $C \times 10^4$. | $\varLambda$. |
|---|---|---|---|---|---|
| 7·659 | 21·10 | 0·9198 | 36·68 | 0·2568 | 44·74 |
| 4·947 | 23·81 | ·6471 | 38·94 | ·2006 | 45·73 |
| 3·399 | 26·64 | ·4975 | 40·86 | ·1240 | 47·84 |
| 2·130 | 29·93 | ·3665 | 42·59 | ·1056 | 48·40 |

### C. Tetra-$iso$-amylammonium Nitrate.

| $C \times 10^4$. | $\varLambda$. | $C \times 10^4$. | $\varLambda$. | $C \times 10^4$. | $\varLambda$. |
|---|---|---|---|---|---|
| 4·706 | 28·18 | 0·6723 | 45·28 | 0·1680 | 54·39 |
| 2·155 | 34·96 | ·6428 | 45·75 | ·1480 | 55·03 |
| 1·407 | 38·80 | ·4073 | 49·05 | ·04873 | 59·02 |
| 1·281 | 39·67 | ·2789 | 51·70 | ·02584 | 60·45 |
| 1·011 | 41·77 | ·2637 | 52·03 | ·01310 | 61·24 |

TABLE VI.—D. Tetra-$n$-butylammonium Nitrate.

| Series, No. | $C \times 10^4$. | $\varLambda_{obs}$. | $f$. | $\gamma$. | $\varLambda_{calc}$. | $100(\varLambda_0 - \varLambda_c)/\varLambda_0$. |
|---|---|---|---|---|---|---|
| I, 1 | 0·6951 | 46·86 | 0·8376 | 0·7675 | 46·82 | +0·09 |
| 2 | ·5307 | 49·14 | ·8536 | ·7997 | 49·12 | +0·04 |
| 3 | ·4102 | 51·10 | ·8678 | ·8269 | 51·16 | −0·12 |
| 4 | ·3099 | 53·18 | ·8818 | ·8558 | 53·21 | −0·06 |
| II, 1 | 26·70 | 17·11 | — | — | — | — |
| 2 | 18·18 | 19·76 | — | — | — | — |
| 3 | 12·42 | 21·81 | — | — | — | — |
| 4 | 7·258 | 25·79 | 0·6503 | 0·4336 | 25·83 | −0·15 |
| 5 | 4·263 | 30·24 | ·7011 | ·5270 | 30·18 | +0·20 |
| 6 | 2·299 | 35·88 | ·7537 | ·6078 | 35·77 | +0·30 |
| 7 | 1·144 | 42·46 | ·8056 | ·7023 | 42·34 | +0·28 |
| 8 | 0·4270 | 50·72 | ·8660 | ·8227 | 50·86 | −0·28 |
| III, 1 | 1·148 | 42·29 | ·8058 | ·7018 | 42·31 | −0·04 |
| 2 | 0·2375 | 54·95 | ·8945 | ·8803 | 55·02 | −0·13 |
| 3 | ·1094 | 59·13 | ·9247 | ·9340 | 59·02 | +0·18 |
| 4 | ·05816 | 61·19 | ·9436 | ·9617 | 61·17 | +0·03 |
| 5 | ·02940 | 62·60 | ·9590 | ·9745 | 62·64 | −0·06 |
| 6 | ·01550 | 63·69 | ·9698 | ·9873 | 63·36 | +0·52 |

[8] We are indebted to Mr. William F. Luder for carrying out these measurements.

were carried out with each salt, but they are recorded separately only in the case of tetra-*n*-butylammonium picrate in anisole (III, D) and tetra-*n*-butylammonium nitrate in ethylene chloride (VI,). In Table III., D are given observed and calculated values of equivalent conductance together with differences; in Table IV., D values of the activity coefficient $f$ and of the degree of dissociation $\gamma$ are given in addition to observed and calculated conductances. (The basis of the calculations will be found in the discussion.) Concentrations are expressed in moles per litre of pure solvent; at the low concentrations of the measurements, neglect of density change due to the solute causes only a negligible error.

## Discussion.

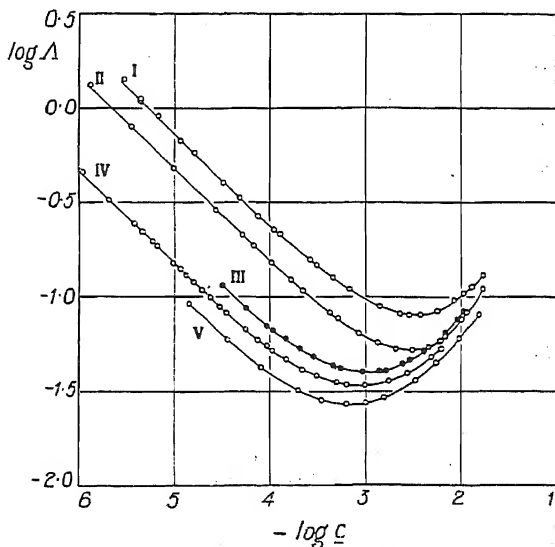The results for anisole and ethylene bromide are shown graphically in Fig. 1, where the logarithms of concentration and of equivalent conductance are plotted as abscissas and ordinates, respectively. In all cases, the curves at lower concentrations approach a slope $d \log \Lambda / d \log C = -1/2$. When the degree of dissociation of the electrolyte is small in comparison with unity, this slope corresponds to a mass action equilibrium between ions and ion pairs. In the neighbourhood of $10^{-3}N$, or above, a minimum appears and the conductance curve rises sharply toward higher concentrations. The minimum is displaced toward higher concentrations as the electrolytes become stronger; compare, for example, the picrate (curve II) with the bromide (curve V).



Fig. 1.—Conductance curves for $Bu_4N \cdot NO_3$ in ethylene bromide (I), and for $Bu_4N \cdot Pi$ (II), $Bu_4N \cdot SCN$ (III), $Bu_4N \cdot NO_3$ (IV) and $Bu_4N \cdot Br$ (V) in anisole.

While the plot is not sensitive to small errors, it nevertheless shows that the experimental results obtained in different series under varying conditions of concentration change (by dilution or by concentration) are in agreement. Sorption effects appear in the more dilute solutions of tetra-*n*-butylammonium nitrate in anisole and ethylene bromide and of the corresponding picrate in anisole (curves IV, I and II, respectively). In the case of the nitrate in anisole, desorption effects were eliminated as has already been explained. Although the individual points deviate considerably from the theoretical curve, due, without doubt, to the fact that these were the first solutions to be measured, the deviations at low concentrations are no greater than at higher concentrations and there is a complete absence of trend over the whole course of the curve.

It is of interest to note that the Shallcross high resistance coils gave satisfactory results. Series 2 for tetra-$n$-butylammonium picrate in anisole was carried out in cell 1 and covered a resistance range from $3\cdot2 \times 10^5$ to $2\cdot3 \times 10^6$ ohms, while series 3 was carried out in cell 4, covering a resistance range from $2\cdot0 \times 10^4$ to $1\cdot5 \times 10^5$ ohms. The two series are in agreement within the limits of experimental error, showing that with proper resistances reliable values of the conductance may be obtained for total resistances up to several megohms.

The conductance curves for solutions in ethylene chloride are shown in Fig. 2, equivalent values of the conductance being plotted as ordinates against the square roots of concentration as abscissas. It will be noted that the curves begin to approach the Debye-Hückel-Onsager slope at concentrations below $5 \times 10^{-6}N$ although, even at the lowest concentrations
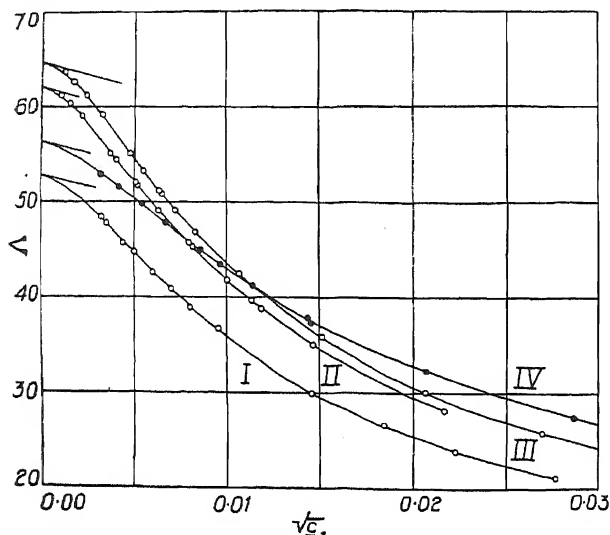


FIG. 2.—Conductance curves in ethylene chloride:
I, $Bu_4N . Ac$ ; II, $i$-$Am_4N . NO_3$ ; III, $Bu_4N . NO_3$ ; IV, $Bu_4N . Pi.$

measured, the deviations from this slope are large. There is a considerable range of concentration over which the curves are approximately linear, but the slope in these regions is primarily determined by the equilibrium between free ions and ion pairs rather than by the ion-atmosphere effect.

As Fuoss and Kraus [2 (III) and (IV)] have pointed out, in the dielectric constant range from 10 to 20, it is necessary to take into account the equilibrium between free ions and ion pairs according to the equation :

$$A^+ + B^- = AB. \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

In solvents of lower dielectric constant, such as anisole and ethylene bromide, equilibria between ion pairs, free ions and triple ions, according to the equations :

$$AB + A^+ = ABA^+$$

and

$$AB + B^- = BAB^-, \qquad . \qquad . \qquad . \qquad . \qquad (2)$$
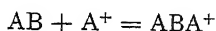
also have a marked influence, even at very low concentrations.

Equilibrium (1) accounts for the rapid falling away of the equivalent conductance below values demanded by the Debye-Hückel-Onsager

slope, as in the case of ethylene chloride, and for the linearity of the curves in the log $\Lambda$—log $C$ plot for solutions in anisole and ethylene bromide. The equilibria (2) account for the deviation of the curves from linearity in dilute solutions and for the minima at higher concentrations.

If $K$ is the constant of equilibrium (1) and $k$ is the constant of equilibria (2) (assumed to be the same for the two reactions), then the conductance may be represented as a function of concentration by the equation : [2] (IV)

$$\Lambda c^{\frac{1}{2}} g = \Lambda_0 K^{\frac{1}{2}} + \lambda_0 K^{\frac{1}{2}} (1 - \Lambda/\Lambda_0) c/k$$

where

$$g = \frac{\exp \left(- \beta' \Lambda_0^{-\frac{1}{2}} c^{\frac{1}{2}} \Lambda^{\frac{1}{2}}\right)}{(1 - \alpha \Lambda_0^{-\frac{3}{2}} c^{\frac{1}{2}} \Lambda^{\frac{1}{2}})(1 - \Lambda/\Lambda_0)^{\frac{1}{2}}}.$$

Here $\alpha$ is the coefficient of the limiting conductance equation and $\beta (\beta = 0.4343 \beta')$ is the coefficient of the limiting activity equation. $\Lambda_0$ and $\lambda_0$ are the limiting conductances of simple ions and triple ions, respectively. Plotting $g \Lambda C^{\frac{1}{2}}$ as ordinates against $C$ as abscissas, a linear graph results ; its intercept on the axis of ordinates gives the product $\Lambda_0 K^{\frac{1}{2}}$ and its slope yields the value of the coefficient $\lambda_0 K^{\frac{1}{2}}/k$. The parametrs $\Lambda_0$ and $\lambda_0$ cannot be determined experimentally in solutions of low dielectric constant, but they may be approximated by means of Walden's rule, which states that the product of equivalent conductance
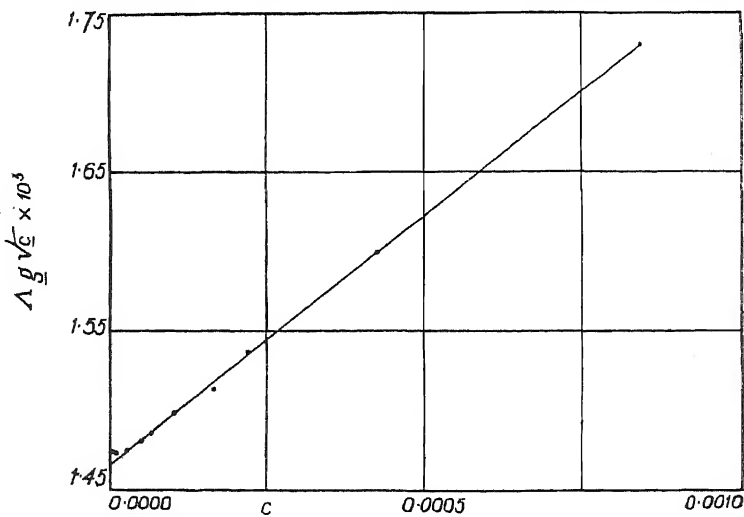


FIG. 3.—Test of the triple ion equation for $Bu_4N$ . Pi in anisole.

and viscosity $(\Lambda_0 \eta)$ for a given electrolyte in different solvents is constant. For determining values of $\Lambda_0$ in anisole, we have values of $\Lambda_0 \eta$ for several electrolytes in ethylene chloride from our own measurements. In the case of other electrolytes, we have approximated $\Lambda_0$ (for ethylene chloride) by comparison with analogous electrolytes (tetraethylammonium salts in methyl alcohol) as measured by Unmack, Bullock, Murray-Rust and Hartley.[9] The viscosities employed were : ethylene chloride,

[9] Unmack, Bullock, Murray-Rust and Hartley, *Proc. Roy. Soc.*, 1931, **132A,** 427.

0·00785 ; anisole, 0·01027 ; ethylene bromide, 0·01570. Values of $\Lambda_0$ computed for anisole are given in Table VII.

TABLE VII.—VALUES OF $\Lambda_0$ IN ETHYLENE CHLORIDE AND IN ANISOLE.

| Salt. | $\Lambda_0(C_2H_4Cl_2)$. | $\Lambda_0\eta(C_2H_4Cl_2)$. | $\Lambda_0(C_7H_8O)$. |
|---|---|---|---|
| $Bu_4N . NO_4$ .   .   .   . | 64·7* | 0·5081 | 49·47 |
| $Bu_4N . SCN$   .   .   . | 64·7 | 0·5081 | 49·47 |
| $Bu_4N . Br$   .   .   . | 61·6 | 0·4837 | 47·09 |
| $Bu_4N . Pi$   .   .   . | 56·3* | 0·4420 | 43·03 |
| $Bu_4N . NO_3$ .   .   .   . | 64·7* | 0·5081 | 31·80† |

Values of $\lambda_0/\Lambda_0$ for tetrabutylammonium nitrate and picrate in anisole have been calculated by Bien, Kraus and Fuoss [6] from conductance measurements in anisole at different temperatures and found to be 0·82 and 0·50 respectively. We have assumed that for the bromide and the thiocyanate $\lambda_0/\Lambda_0$ has the same value as for the nitrate.

In Table VIII. are given values of the dissociation constants $K$ and $k$ for the various electrolytes in anisole (based on $\Lambda_0$ values of Table VII.). Following the method of Fuoss and Kraus,[2 (III) and (IV)] we have also calculated the parameters $a$ and $a_3$, which may be interpreted respectively as the mean distance between centers of charge of two ions in an ion pair and in a triple ion. These values for $a$ and $a_3$ are given in the table.

TABLE VIII.—CONSTANTS OF ELECTROLYTES IN ANISOLE AND ETHYLENE BROMIDE.

| Salt. | $\Lambda_0$. | $K \times 10^{10}$. | $a \times 10^8$. | $k \times 10^4$. | $a_3 \times 10^8$. |
|---|---|---|---|---|---|
| $Bu_4N . Br$   .   . | 47·1 | 0·491 | 4·61 | 4·64 | 5·43 |
| $Bu_4N . NO_3$   .   . | 49·5 | ·865 | 4·94 | 6·10 | 5·69 |
| $Bu_4N . SCN$   .   . | 49·5 | 1·55 | 5·06 | 8·49 | 6·02 |
| $Bu_4N . Pi$   .   . | 43·0 | 11·6 | 5·61 | 23·4 | 8·20 |
| $Bu_4N . NO_3‡$   .   . | 31·8 | 47· 9 | 5·34 | 25·8 | 6·69 |

As may be seen from the table, the strength of the electrolytes measured in anisole solution increases in the order : bromide, nitrate, thiocyanate, picrate. While the precise nature of the ions in solution is not known, since solvation may occur, the results are in accord with the view that the dissociation of electrolytes is the greater the larger their ions.[10] The parameter $a$ (distance between charges) naturally follows the order of dissociation constants and the values obtained seem reasonable from the point of view of atomic dimensions.

The dissociation constant of tetrabutylammonium nitrate in ethylene bromide is approximately fifty times that in anisole. This larger value of $K$ is in part due to the larger dielectric constant of ethylene bromide and in part to the larger size of the ions in the latter solvent. There

[10] Compare Kraus and Hawes, *J. Amer. Chem. Soc.*, 1933, **55**, 2776 ; Kraus and Johnson, *ibid.*, 1933, **55**, 3542.

    * Experimentally determined.           † In ethylene bromide.
    ‡ In ethylene bromide.

is evidence indicating that the size of an ion is dependent on the solvent medium.    In ethylene chloride the ions of tetrabutylammonium nitrate are smaller than in ethylene bromide and larger than in anisole ; values of $a$ are $5 \cdot 10 \times 10^{-8}$ (Table IX.), $5 \cdot 34 \times 10^{-8}$ and $4 \cdot 94 \times 10^{-8}$, respec-tively.

The parameter $a_3$, which may be looked upon as the effective diameter of the ions in the triple ion formation, is uniformly greater than that of the parameter $a$.    This is perhaps not surprising, since the ions are by no means true spheres and one should expect that the statistical equi-librium would be influenced by the shape as well as by the size of the ions.    This applies, in particular, to the picrate ion where the charge is obviously located on the phenolic oxygen atom of the ion.    At any rate, the value of $a_3$ for the picrate is exceptionally high, indicating a low degree of stability of the triple ions.    Since the minimum in the conductance curve is determined by the value of the triple ion dis-sociation constant, the minimum for the picrate lies at a relatively high concentration.    This property of the picrate is also found in its solutions in benzene.[2 (V)]    The order of the triple ion dissociation constant follows that of the ion pair constant for the electrolytes appearing in Table VIII.

The constants given in the table reproduce the experimental con-ductance values closely.    To illustrate the agreement between experi-mental and calculated values and to indicate the adequacy of the treat-ment, the results for tetrabutylammonium picrate in anisole are shown graphically in Fig. 3, values of $g \Lambda C^{\frac{1}{2}}$ being plotted as ordinates against concentrations as abscissas.    If our assumptions are correct, the experimental points should lie on a straight line.    The radii of the circles which represent the experimental points are drawn with a diameter corresponding to an experimental error of $0 \cdot 1$ per cent.

In Table III. D, observed and calculated values (based on constants of Table VIII.) of the equivalent conductance are compared for the picrate in anisole.    Between the concentrations $8 \cdot 4 \times 10^{-4}$ and $2 \cdot 7 \times 10^{-5}$, observed and calculated values agree within $0 \cdot 1$ per cent. with the exception of the first point in series 3 where the deviation is $0 \cdot 4$ per cent.    This discrepancy is doubtless due to an accidental experimental error.    The observed value of point 4, series 3, at a con-centration of approximately $1 \times 10^{-5}N$, is $0 \cdot 22$ per cent. high and the discrepancy between observed and calculated values increases markedly with points 5 and 6 where the concentration approaches $1 \times 10^{-6}N$. These deviations are due to desorption, since no precautions were taken to eliminate this effect in the case of these solutions.    We may say, therefore, that between approximately $1 \times 10^{-3}$ and $1 \times 10^{-5}N$, observed and calculated values agree within $0 \cdot 1$ per cent.    This indicates, on the one hand, that the experimental results are satisfac-torily accounted for by means of the mechanism assumed and, on the other, that the experimental values are reproducible within $0 \cdot 1$ per cent.

In the case of solutions in ethylene chloride, only the equilibrium (1) needs to be taken into account.    The experimental data were treated analytically by the method of Fuoss and Kraus [2 (II)] and values of $\Lambda_0$ and of $K$ were determined.    Values of the parameter $a$ were computed from values of $K$.    The values of these constants are presented in Table IX.

Electrolytes whose ions approximate the assumed spherical model are the more dissociated the larger their ions and hence the lower the mobility of their ions.    Thus the picrate is a markedly stronger electro-lyte ($K = 2 \cdot 56 \times 10^{-4}$) than the corresponding nitrate ($K = 1 \cdot 23 \times 10^{-4}$).

The acetate, on the other hand, is a weaker electrolyte than the picrate, although the mobility of the acetate ion is lower than that of the picrate ion. The low mobility of the acetate ion is doubtless due to association of solvent molecules with the carboxyl group of that ion ; it will be recalled that the acetate ion has an exceptionally low mobility in water.

TABLE IX.—CONSTANTS OF ELECTROLYTES IN ETHYLENE CHLORIDE.

| Salt. | $\Lambda_0$. | $K \times 10^4$. | $a \times 10^8$. |
|---|---|---|---|
| $Bu_4N . NO_3$ | 64·7 | 1·23 | 5·10 |
| $Am_4N . NO_3$ | 62·0 | 1·26 | 5·12 |
| $Bu_4N . Pi$ | 56·3 | 2·56 | 5·92 |
| $Bu_4N . Ac$ | 52·8 | 1·36 | 5·18 |

It seems probable that the solvation of free ions may be greater than that of the ions in the associated ion-pairs. The low dissociation constant of the acetate may be accounted for in this way.

The mobility of the tetra*iso*amylammonium ion is only slightly lower than that of the tetrabutylammonium ion, and there is little difference in the value of the dissociation constants of their nitrates. The values of the parameter $a$ follow the order of the dissociation constants and lie between 5·1 and 5·9 Ångström units. Everything considered, these dimensions seem reasonable ; for a given salt, $a$ is slightly greater in ethylene chloride than in anisole and smaller than in ethylene bromide.

Using values of $K$ and $\Lambda_0$ as given in Table IX., and 10·23 for the dielectric constant of ethylene chloride, conductance values were computed [2 (II.)] for solutions of tetrabutylammonium nitrate. Computed and measured values are compared in Table V. D. The mean deviations for series, 1, 2 and 3 are 0·08, 0·24, and 0·09 per cent., respectively, excluding only the last point of series 3, where it was very difficult to overcome sorption effects. Series 2 is less satisfactory than the other series, probably owing to manipulation errors. Considering the magnitude and persistence of sorption effects below $10^{-5}N$, the results of Series 3 are in excellent agreement with the computed values. Experimental and computed values thus agree within approximately 0·1 per cent. between $7 \times 10^{-4}N$ and $3 \times 10^{-6}N$, a dilution ratio of 1 : 240.

The values given in Table V. D for the activity coefficient $f$ and the dissociation $\gamma$ for solutions of tetrabutylammonium nitrate in ethylene chloride are of interest. Both show large variations ; over the concentration range $1·5 \times 10^{-6}$ to $7·2 \times 10^{-4}$, the variation of $\gamma$ is somewhat greater than that of $f$, although at the lower concentrations, $\gamma$ approaches unity more rapidly than does $f$.

The need for taking into account the effects due to association as well as to ion-atmosphere seems obvious. In solvents of lower dielectric constant, the ion-atmosphere effect becomes smaller while the effect due to ion association increases. At the same time, the phenomena are rendered more complex by other association effects such as the formation of triple ions. In solvents of very low dielectric constant, the ion-atmosphere effect becomes negligible owing to the very low concentrations of ions, while association effects become more complex ; aggregates of higher order are formed containing odd as well as even numbers of ions. These highly complicated association processes determine the course of nearly all measurable properties of solutions of electrolytes in non-polar media.

As the dielectric constant of the solvent medium is lower, the con-

centrations at which the phenomena become sufficiently simple to admit of analysis are likewise lower. At these concentrations, precise measurement of physical properties is rendered difficult, partly due to the small magnitude of the effects to be measured and partly due to the intrusion of new sources of error, such as adsorption. The solution of the problem of electrolytic solutions in its more general form waits the development of more refined experimental technique ; only when reliable data have become available over a wide range of the variables concentration, dielectric constant and temperature may we expect a satisfactory solution of the problem to be forthcoming.

## Summary.

Several sources of error affecting conductance measurements with solutions in solvents of low dielectric constant and at low concentrations have been investigated and means have been devised to eliminate or minimise them.

The conductance of a number of quaternary ammonium salts has been measured in ethylene chloride, ethylene bromide and anisole as solvents. Values reproducible within o·1 to o·2 per cent. have been obtained at concentrations of the order of one-millionth normal.

The experimental values are in accord with the ion association theory, as developed by Fuoss and Kraus, within the limit of experimental error.

The constants of the association equilibria have been evaluated and ion dimensions have been computed therefrom. The dimensions so found are in reasonably good accord with atomic dimensions.

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# THE EFFECT OF TEMPERATURE ON THE PHOTOCHEMICAL DECOMPOSITION OF ACETONE.

BY C. A. WINKLER.

(*Communicated by* C. N. HINSHELWOOD.)

It has been suggested[1] that the thermal decomposition of acetone proceeds by a chain mechanism. Experimental work on the thermal reaction alone, however, contradicts this view.[2,3] It was thought of interest, therefore, to determine whether or not the rate of change of reaction velocity with temperature obeys the Arrhenius relation when acetone is decomposed under the influence of ultra-violet light. While this work was in progress, the results of an investigation directed towards the same end were reported in the literature.[4] It was shown that the

[1] Rice, F. O., and Herzfeld, K. F., *J. Amer. Chem. Soc.*, 1934, **56**, 284.
[2] Rice, F. O., Rodowskas, E. L., and Lewis, W. R., *J. Amer. Chem. Soc.*, 1934, **56**, 2497.
[3] Winkler, C. A. and Hinshelwood, C. N., *Proc. Roy. Soc.—in press.*
[4] Leermakers, J. A., *J. Amer. Chem. Soc.*, 1934, **56**, 1899.

quantum efficiency of the photochemical reaction increased from about 0·3 at 60° C. to unity at a temperature of about 160° C.; from 160° to 400° C. no further increase in quantum efficiency was observed. It was concluded that no chains were initiated in the decomposition of acetone below 400° C. The present investigation supports this conclusion. In addition, however, the results have been fruitful in suggesting a new line of attack in the study of photo-chemical reactions in general.

The reacting gas was contained in a bulb of clear, fused quartz, placed in an electric furnace, one side of which was provided with a quartz window through which the light was admitted to the reaction vessel. The rate of decomposition of the acetone was followed by observing the rate of pressure change on a mercury manometer, with the aid of a cathetometer. No difficulty was experienced in obtaining reproducible results, even when the pressure increased no more than 2 mm. in the course of an hour. Interposition of appropriate filters [5] between the lamp and the reaction bulb permitted illumination of the reacting gas by any desired portion of the mercury arc 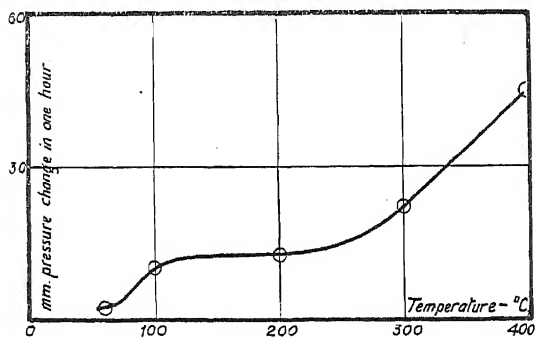spectrum. After each run, the reaction vessel was removed and thoroughly cleaned. Temperatures were controlled within 0·2°, and were measured on mercury thermometers. The constancy of the illumination was checked during each run by determining the amount of decomposition produced simultaneously in a standard uranyl oxalate solution.



FIG. 1.

Determinations of the rate of decomposition were first made with only a water filter interposed between the lamp and the reacting gas. The decomposition was studied at five temperatures,—60°, 100°, 200°, 300°, and 400° C.—the initial *concentrations* of acetone being the same in each case. The relationship between time and pressure increase was practically linear during the first hour at each temperature. Over greater periods of time, the rate fell off somewhat at the higher temperatures, due partly to the diminished concentration of acetone, and partly to the formation of a brown deposit on the inner surface of the reaction vessel. This deposit was not in evidence at 60° and 100° C., and only slightly at 200° C., even after prolonged exposure to the light. At 300° and 400° C., however, the deposit was quite marked after the first hour. A plot of pressure increase during the first hour against temperature is shown in Fig. 1. The values of the pressure increase shown have been obtained by multiplying the observed pressure increase at each temperature, $t$, by the ratio $\dfrac{333}{t + 273}$, so that all values correspond to that at 60° C.

Experiments were also made at 60° and 400° C., using different portions of the mercury arc spectrum to illuminate the gas. It was found that when light of short wave-length was used, the rate of decomposition at

[5] Bowen, E. J., *J. Chem. Soc.*, 1935, 76.

60° C. was considerably greater than when light of long wave-length was used at the same temperature. At 400° C., however, the rate of reaction was greater for the light of long wave-length. The following figures serve to illustrate this fact.

There seems to be little doubt that the rate of decomposition is less influenced by temperature change when light of higher frequencies is the exciting agent.

| Range of Wave-lengths used. | Ratio $\dfrac{\text{Rate at } 400° \text{ C.}}{\text{Rate at } 60° \text{ C.}}$. |
|---|---|
| 2200-2800 Å. (ca) | 18 |
| 3135 line . . | 40 |
| 2800-3300 Å. (ca) | 50 |

An analysis was made on a Bone and Wheeler apparatus of the products obtained from the photochemical decomposition of acetone at 400° C. The results were :

$CO_2$ and $O_2$—0·0 per cent. ; Unsaturated compounds—5·6 per cent. ; CO—40·5 per cent. ; $H_2$—5·0 per cent. ; $CH_4$—32·0 per cent. ; $C_2H_3$—16·6 per cent.

These results should be compared with those for the photochemical decomposition at 60° C., and with those for the thermal reaction at 560° C. At 60° C., the photochemical decomposition yields : [6]
$CO_2$ and $O_2$—0·0 per cent. ; Unsaturated compounds—0·0 per cent. ; $H_2$—0·0 per cent. ; CO—46·6 per cent. ; $CH_4$—9·2 per cent. ; $C_2H_6$—44·2 per cent.

The products for a corresponding amount (about 50 per cent.) of thermal decomposition are [3] :

$CO_2$ and $O_2$—3·6 per cent. ; Unsaturated compounds—11·6 per cent. ; $H_2$—3·0 per cent. ; CO—33·6 per cent. ; $CH_4$—49·0 per cent. ; $C_2H_6$—0·0 per cent.

Absorption measurements were not possible with the type of apparatus used, and any calculations based on the data shown in Fig. 1 must assume no change in the extinction coefficient with temperature. If this assumption is made, and a mean quantum efficiency of 0·3 at 60° C. is taken for the range of wave-lengths used (ca. 2200-3300 Å.) the quantum efficiency at 100° C., calculated from the relative rates of pressure change, is seen to be about 1·5. In view of the uncertainty regarding the relative absorptions at the two temperatures, this value agrees as closely as can be expected with Leermakers' value [4] of unity for temperatures above 160° C. The increase in quantum efficiency from about 0·3 to unity, as the temperature is raised from 60° to 100° C., can be satisfactorily accounted for by a more efficient utilisation of the absorbed energy, due to thermal excitation of the C—C linkages. At temperatures above 300° C., the increased rate of pressure change can not be assumed to mean an increase in quantum efficiency. There is, in fact, little doubt that the quantum efficiency remains unity up to 400° C. The increased rate of pressure change is probably due to increased light absorption and simultaneous decomposition of some substance formed during the photochemical decomposition of acetone at 300°–400° C.

The presence of unsaturated compounds in the products at 400° C., and the deposition of the brown condensate on the wall of the reaction

[6] Norrish, R. G. W., Crone, H. G., and Saltmarsh, O. D., *J. Chem. Soc.*, 1934, 1456.

vessel at 300°-400° C., point to the photochemical formation of ketene from acetone at these temperatures.[7] The high proportion of methane in the products at 400° C. can also be explained in this way.

While the formation of ketene could be accounted for on the basis of the free radical theory by assuming decomposition of the $CH_2COCH_3$ radical,—a process which Leermakers considers improbable—there is no reason why ketene should not be formed in the primary photochemical act at 300°-400° C. If ketene is formed in the primary act at high temperatures, the manner in which the absorbed quantum is utilised must be considerably different from that at 60° C. At 60° C., regardless of whether or not the primary act produces free methyl radicals, the products obtained show that the fraction of the absorbed energy which results in rupture of the molecule is utilised predominantly in breaking the C—C linkages. The primary formation of ketene at higher temperatures, however, requires utilisation of the absorbed energy in breaking a C—H bond. It is not unreasonable to expect this to occur when the molecule is thermally excited.

The different temperature coefficients of reaction velocity with different wave-lengths is another important factor which must be considered in connection with the utilisation of energy in decomposing a complex molecule such as acetone. This variation might be due to different temperature coefficients of the absorption coefficients for waves of different frequencies. If the absorption coefficient for longer waves increases more rapidly with temperature than for shorter waves, the effect would be similar to that observed. It is quite improbable, however, that an effect as large as that observed can be satisfactorily explained in this way. It is suggested, therefore, that the efficiency with which a quantum of small energy content is utilised in the act of decomposition increases much more rapidly with increase of temperature than the efficiency with which a larger quantum is utilised. In the absence of thermal excitation, a large quantum might well be sufficient to decompose a molecule, while a smaller quantum would be insufficient. When the molecule becomes thermally excited, however, small quanta might be as effective as large quanta in bringing about decomposition. If this is true, the rate of reaction would increase more rapidly with temperature when light of long-wave length is used. Furthermore, in a molecule which has been thermally excited to a limited extent, a large quantum might be capable of bringing about a primary photochemical act different not only from that which it can initiate at lower temperatures, but different also from that which a smaller quantum can bring about at the higher temperature. The primary photochemical act might, therefore, be a function, not only of temperature, but also of the frequency of the exciting light.

The validity of the suggestions put forward in this communication can only be tested by further experimental work. Whether or not they are found to be correct, the line of attack indicated promises to furnish much useful information concerning photochemical reactions themselves, and their relationship with thermal reactions.

[7] Ross, W. F., and Kistiakowsky, G. B., *J. Amer. Chem. Soc.*, 1934, **56**, 1112.

He wishes to thank Mr. E. J. Bowen also for numerous helpful suggestions, and for the loan of apparatus.

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# THE SURFACE POTENTIALS OF AQUEOUS SOLU-TIONS OF OCTYL ALCOHOL AND CAPRYLIC ACID.

By Ikutaro Sawai.

The "surface potential," that is, the change in contact potential at the air-liquid surface of water, caused by the presence of a dissolved substance or a surface film, has usually been measured for *solutions* of capillary active substances by the method of flowing jets, in which one liquid flows in a jet down the centre of a tube, the other in a film distributed as evenly as possible over the inside wall of the tube. This method was used by Kenrick,[1] and extensively applied by Frumkin,[2] to the study of the surface potentials of both inorganic and organic solutes. For *insoluble* surface films, this method is not applicable, as the motion of the flowing liquids would disturb the surface films ; also for solutions of capillary active substances, where adsorption is not practically instantaneous, erroneous results may be obtained. For insoluble films, the usual practice has been to employ an insulated air electrode, consisting of a metal plate or wire coated with a small amount of a radioactive substance, such as polonium, which ionises the air and permits the air electrode to maintain a steady potential, determined by the contact potentials at the surfaces. This method was introduced, for air-liquid surfaces, by Guyot,[3] and has been extensively used by Frumkin,[4] Schulman and Rideal,[5] Harding and Adam,[6] and many others. In this work a simple method for using the air electrode covered with polonium, with solutions of capillary active substances, has been used.

## Experimental.

The arrangement of the apparatus is shown in Fig. 1. The air electrode A, held on an insulating silica rod, is kept about a millimetre above the liquid surface, which is at the rim of a funnel B, 5 cm. diameter. The whole apparatus was encased in an earthed metallic cage, to avoid accidental electrical disturbances. The liquid in the funnel communicated through capillary tubing with a reservoir D, above the level of the rim of the funnel, thence through a bent tube E filled with the same liquid, the ends of this tube being roughly stoppered with filter paper, with a tube F

[1] *Z. physikal. Chem.,* 1896, **19,** 625.
[2] *Ibid.,* **109,** 34 ; **111,** 190, 1924.
[3] *Ann. Physique* (10), 1924, **2,** 531.
[4] *Z. physikal. Chem.,* 1925, **116,** 485.
[5] *Proc. Roy. Soc.,* 1931, **130A,** 259.
[6] *Trans. Faraday Soc.,* 1933, **29,** 837.

containing normal potassium chloride solution.   A normal calomel half cell G, dipping into F, formed the negative end of the electrical chain.   An electrometer triode and potentiometer were used to record the e.m.f. of the whole cell,

Hg/HgCl/KCl N/experimental solution/air/air electrode,

all connections being made as described by Harding and Adam.[6]

The container D and the funnel F must be kept throughly clean ; they



FIG. 1.

were kept in chromic acid when not in use, and washed several times with the experimental solution before taking readings.   A little of the solution was allowed to overflow the edge of the funnel so as to carry away any traces of grease accidentally present. The solution was introduced by pouring into the funnel and sucking into D up to a fixed mark.   The tap C served for drainage.

The apparatus was not thermostated, but the temperature was always within 2° of 18° C.

The readings obtained were liable, under the best conditions, to fluctuations of from 2 to 5 millivolts ; successive readings of fresh solutions could be reproduced within 10 millivolts, provided the apparatus was clean.

The caprylic acid was fractionally distilled, the fraction boiling at 222-223° C. (corr.) being taken ; this was frozen and partially melted at room temperature, the liquid being absorbed by pressing between filter papers. The purified acid melted at 15·5°-16·0° C.   $n$-Octyl alcohol from British Drug Houses, Ltd., was fractionally distilled three times ; b.p. 195° (conc.) ; density, 0·8243 at 25° C.

The e.m.f. of the whole cell was found to depend in the following way on the concentration of hydrochloric acid, when this alone was used as the experimental solution.

The e.m.f. of the cell, using solutions of caprylic acid in various strengths of hydrochloric acid, or of sodium caprylate in caustic soda, were next measured.   The results are shown in Fig. 2, the concentrations of caprylic acid or sodium caprylate being plotted as abscissæ, and the difference between the e.m.f. of the cell containing the caprylic acid, and that of the cell containing the same strength of hydrochloric acid, but without the caprylic acid, as ordinates. This difference is probably almost entirely due to the adsorbed surface film at the air liquid surface, and is called the surface potential $\Delta V$.

| Concentration. | E.m.f. |
|---|---|
| 5 $N$ | − 639·0 |
| 4 $N$ | − 580·5 |
| 3 $N$ | − 368·3 |
| 2 $N$ | − 249·5 |
| 1 $N$ | − 244·5 |
| 10⁻⁴ $N$ | − 295·8 |

There is a rapid increase in surface potential as the concentration increases, up to about $5 \times 10^{-4}$ molar, and thereafter a more gradual increase.   The concentration of the hydrochloric acid, also, has a considerable effect.   As the hydrochloric acid concentration increases from $10^{-4}$ normal to $10^{-2}$ normal, the surface potential increases by about 80 millivolts.   There is no detectable change between 0·01 $N$ and normal hydrochloric acid, but a very considerable increase in surface potential again, about 100 millivolts, when the hydrochloric acid concentration was further increased to 4 $N$.   In all cases the sign of the surface potential
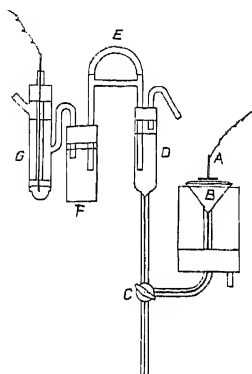
was such that the caprylic acid rendered the outer surface more positive. It seems probable that the lower surface potentials in the most dilute solutions of hydrochloric acid are due to the adsorbed film of caprylic acid being electrolytically dissociated to some extent ; in normal, and 0·01 $N$ hydrochloric acid, the dissociation is probably completely suppressed. In the strong, 4 $N$ hydrochloric acid the further increase in surface potential is probably an effect of the same nature as that observed by Schulman and Hughes,[7] who found with insoluble acids and alcohols a very considerable increase of surface potential on 4 $N$ hydrochloric acid solutions, and ascribed it to the formation of an oxonium salt with one of the oxygen atoms in the carboxyl group.

The two lowest curves show the surface potentials found with solutions of sodium caprylate in normal and $N/100$ caustic soda. A prac-
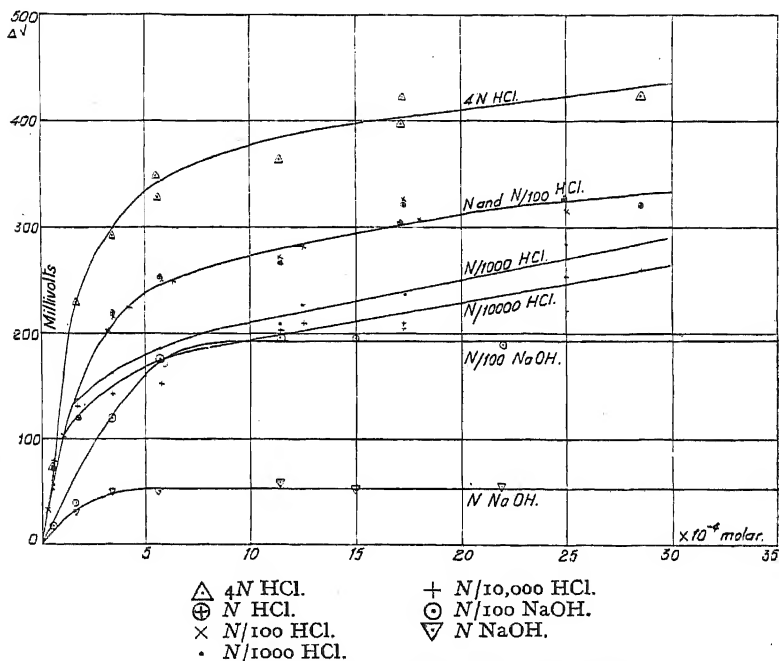


FIG. 2.—Surface potential of caprylic acid solutions.

| | |
|---|---|
| △ 4$N$ HCl. | + $N/$10,000 HCl. |
| ⊕ $N$ HCl. | ⊙ $N/$100 NaOH. |
| × $N/$100 HCl. | ▽ $N$ NaOH. |
| · $N/$1000 HCl. | |

tically constant surface potential was reached at all concentrations greater than $8 \times 10^{-4}$ molar. The surface potential in the normal sodium caprylate was little more than a quarter of that in the hundredth normal solution. It seems probable that the greater concentration of sodium ions in the stronger solution causes the double layer in the surface, which consists of carboxyl groups uppermost and sodium ions below, to decrease in thickness ; thus the length of the dipoles in the surface, perpendicular to the surface, decreases, and the contribution of a single molecule to the surface potential diminishes.

Fig. 3 shows similar results obtained with solutions of octyl alcohol. The strength of hydrochloric acid is apparently without effect, from very dilute solutions up to the normal ; there is, however, again an increase

[7] *Proc. Roy. Soc.*, 1932, **138A**, 430.

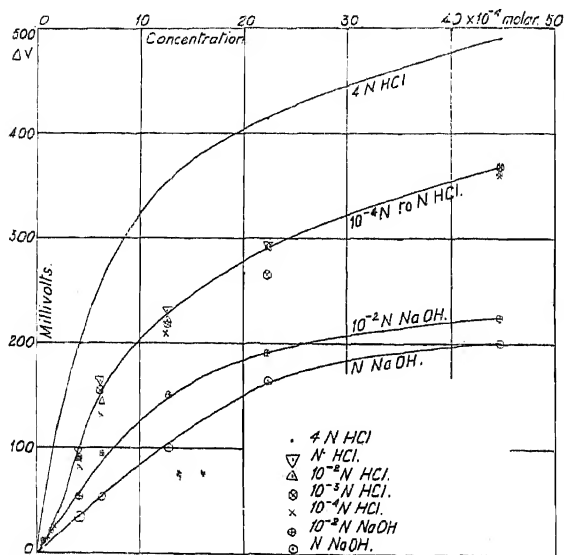of surface potential of slightly over 100 millivolts on increasing the concentration to 4 $N$. This may also be due to the formation of an oxonium salt with the oxygen atom of the molecules in the adsorbed surface film. Alkali decreases the surface potential considerably, the difference between normal and 0·01 $N$ being in the same d i r e c t i o n, but much smaller, than with caprylic acid.



FIG. 3.—Surface potential of $n$-octyl alcohol solutions.

In order to obtain the fullest possible information as to the meaning of these changes in surface potential, the number of molecules per square centimetre of the film should be ascertained. Some preliminary results, obtained by measuring the surface tension of the solutions by Sugden's modification of the maximum bubble pressure method, and calculating the area per molecule by Gibbs' adsorption equation, assuming the activity coefficient of the caprylic acid and octyl alcohol to be unity, indicate that the values of $\mu$, calculated from the equation:

$$\Delta V = 4\pi n\mu$$

($\Delta V$ = surface potential, $n$ the number of molecules per sq. cm.) are of the order of magnitude indicated below :

The surface tension measurements were hardly accurate enough, however, for the above figures to be reliable to closer than one or two units, nor is it certain whether there is any progressive change

| Substance. | Solution. | (e.s.u. $\times 10^{-10}$). |
|---|---|---|
| Caprylic acid | 4 $N$ HCl | ca. 5 |
| ,,    ,, | $N$ and 0·1 $N$ | ,,  2·8 |
| ,,    ,, | 0·001 $N$ and 0·00001 $N$ | ,,  2·5 |
| ,,    ,, | 0·01 $N$ NaOH | ,,  12 |
| ,,    ,, | $N$ NaOH | ,,  4 |
| Octyl alcohol | 4 $N$ HCl | ,,  6 |
| ,,    ,, | N to 0·00001 $N$ HCl | ,,  4 |
| ,,    ,, | 0·01 $N$ NaOH | ,,  2·7 |
| ,,    ,, | $N$ NaOH | ,,  2·2 |

in $\mu$ as the solution becomes more concentrated and the number of molecules in the surface film increases. It is hoped to proceed to more accurate determinations of the area per molecule in the adsorbed films soon.

## Summary.

An apparatus for the measurement of the surface potential of solutions by the use of an air electrode coated with radioactive material is described. The surface potentials of caprylic acid and of octyl alcohol have been measured in dilute solution in various strengths of hydrochloric acid and caustic soda.

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# QUICKSAND AS A THIXOTROPIC SYSTEM.

By H. Freundlich and F. Juliusburger.

*Received 11th March,* 1935.

Sea sand has a tendency to form a closely packed system; the grains approach one another very closely, enclosing only a small volume of liquid. It therefore shows generally very distinctly the so-called Osborne Reynolds phenomenon, to use his terminology, dilatancy; *i.e.*, it becomes harder and dryer when dislocated, for instance by the step of the foot, and returns to its original state of moisture as soon as external forces cease to act. Dilatancy is only found in systems in which the particles are closely packed.[1] Now smaller or larger regions of a coast are known, which may be covered with " quicksand," a sand remarkable because it shows the opposite behaviour: it seems fairly firm, but becomes soft and liquid when dislocated. Quicksand has roused interest for centuries, but the dangers caused by its treacherous behaviour seem to have captivated the imagination of poets rather than that of scientists. It is surprising how little has been said and done to explain the extraordinary behaviour of quicksand.

The only explanation put forward is that the mobile state of the sand is due to currents of water, rising through the sand or traversing it.[2] This may be valid in some, perhaps in many, cases; for it has been shown that a mixture of fine sand and water may flow under suitable conditions.[3]

There is, however, another possibility, as was pointed out by Professor F. G. Donnan; may not quicksand be thixotropic, *i.e.*, may it not be a very loosely packed system containing a high amount of fluid, which

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[1] Osborne Reynolds, *Phil. Mag.* (5), 1885, **20**, 469; *Nature*, 1886, **33**, 429. Spring (*Bull. Soc. Belg. geol.*, 1903, **17**, No. 13) made the following experiment: he allowed a fine, purified sand with a particle size of 5-10$\mu$ to take up water through a pig's bladder, until a state of equilibrium was reached. The volume filled with water was 26·3 per cent. of the whole sand. In the case of closest packing it ought to be 26 per cent.

[2] *Cf.* for instance W. G. Mead, *J. Geology*, 1925, **33**, 692.

[3] Spring, *loc. cit.*[1]

will flow on shaking or other mechanical treatment, but return to a distinctly firm, paste-like condition when at rest ?   Loose packing would be a static phenomenon in this case, not a dynamic one as when it is due to streaming water.   It would be easy to distinguish between these two possibilities : if quicksand is thixotropic, small samples of the sand investigated in a test-tube would still behave like the bulk of the sand in its natural surroundings ; this would not be the case if the mobile state of quicksand were caused by streaming water.

Now a thixotropic behaviour of quicksand would be curious.   The particle size of normal sand is generally so great (above $10\mu$) that thixo-tropy appears very improbable.   According to our experiments a marked percentage of the particles must have diameters down to $1\mu$ in order that the mass may become thixotropic.[4]   Finely powdered quartz, having a high percentage of particles between $1$ and $10\mu$, is indeed thixotropic in sea water ; it is not so in pure water.   But it did not seem very pro-bable that quicksand had such small particles.   On the other hand this finely powdered quartz, not being thixotropic in pure water, may be made so by adding substances such as lecithin [5] or clay, and a similar behaviour is known in the case of other natural, non-thixotropic systems, which turn thixotropic when a suitable colloid is added.   We, therefore, were led to ascribe a possible thixotropy of quicksand to an admixture of foreign substances (clay, organic matter, etc.).

Thanks to the courtesy of Professor P. G. H. Boswell of the Royal School of Mines, we came in touch with Dr. J. T. Jenkins from the Lancashire and Western Sea Fisheries Joint Committee, to whose kind-ness we are greatly indebted for the samples of quicksand we were able to investigate.   We had the following samples : 1. quicksand from Knott End, Fleetwood ; 2. ordinary sand, taken about 50 yards away from where the quicksand was taken ; 3. quicksand from Southport ; 4. ordinary sand from there ; 5. quicksand from New Brighton, Cheshire ; 6. ordinary sand from there.

The quicksand from Knott End, Fleetwood, happened to be distinctly thixotropic.   A mixture of 3 g. quicksand + 1·4 c.c. sea water,[6] shaken in a test tube, was mobile ; left to rest a certain time, it solidified ; the test-tube could be turned upside down without the mass flowing down. The time of solidifying was about 5 to 10 minutes.   Ordinary sand (sample 2) of the same degree of moisture is practically always a hard clod.   It does not flow, and when the tube is reversed only a certain amount of aqueous solution flows out, practically without any movement of the grains of sand.   The following behaviour is also characteristic : if the tube with the settled quicksand is turned upside down and then tapped gently with the fingers, the whole mass flows down covering the walls of the tube uniformly.   Ordinary sand treated in the same way remains a hard clod, only a small number of grains being dislocated.   The ordinary sand showed on the other hand pronounced dilatancy.   Brought on to a watch glass and compressed, pushed with a spatula into a heap, it turns hard and dry, and when left to itself exudes water again slowly or more quickly if by gently tapping the glass the particles are induced more rapidly to assume their original close packing.   The quicksand

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[4] *Cf.* as to the following paragraph Freundlich and Juliusburger, *Trans. Farad. Soc.*, 1934, **30**, 333.

[5] Freundlich, *J. Soc. Chem. Ind.*, 1934, **53**, 223 T.

[6] In many cases the samples with sea water were made up by mixing sand, evaporated to dryness, with pure water.

treated in the same way may be spread over the glass more easily, exerting much less resistance towards any deformation. It nevertheless still shows dilatancy to a certain extent, when containing a smaller amount of moisture, though less distinctly than the ordinary sand. This case lying on the border-line of loose packing will be discussed somewhat more fully later on.

From the outset it was evident that the quicksand contained foreign substances. It has a different colour, being dark greyish brown, whereas the ordinary sand is light yellowish brown. When both sands are shaken in an excess of water and then left to settle, the grains of the ordinary sand are deposited rapidly, the liquid above being only slightly turbid. In the case of the quicksand the fluid above the grains remains quite opaque for a long time. The substance suspended is obviously a very fine clay. It was separated from the quicksand by washing, in such a way that all particles with diameters below $5\mu$ belonged to this clay fraction. It was a very plastic mass showing all the properties of clay. After drying, it formed a beautifully coherent sheet which, when rolled together, looked like a dark grey tobacco leaf. After ignition it remained coherent and had the structure of a pinkish brown film of earthenware. The quicksand contained about 2·1 per cent. of this clay, whereas the ordinary sand only had about 0·3 per cent. The clay was rich in iron ; analysed quantitatively, it contained 47 per cent. $SiO_2$ ; 14·4 per cent. $Al_2O_3$ ; 13·9 per cent. $Fe_2O_3$ ; loss by ignition 15·5 per cent. ; the residue consisted of alkalis and traces of calcium. When seeking to correlate these figures with the formula of a mineral, it must be borne in mind that we do not know whether we have really obtained a chemical entity by the method of separation used. But the fairly high amount of $SiO_2$ suggests a clay-like substance.

The following facts prove that the thixotropic behaviour of the quicksand was chiefly due to the presence of this clay. The quicksand, separated from the clay, care being taken to eliminate all particles with a diameter of less than $10\mu$, had the properties of ordinary sand : it was not thixotropic, and showed stronger dilatancy. It also had lost its dark greyish colour, and assumed the lighter colour of ordinary sand. On the other hand, if the clay was added again to the residue of the quicksand, this mixture acquired thixotropic properties and its dilatancy was feebler. The fact that the whole mass of the quicksand looks darker than the ordinary sand makes it probable that the grains of quicksand are all covered by the clay. And this strongly hydrophilic layer, having most probably a certain swelling capacity, is instrumental in producing that loose packing which causes thixotropy.

It hardly needs to be stated that this clay, in the right state of moisture, is strongly thixotropic. When spread over a watch-glass it, also, is absolutely plastic like butter and shows no sign of dilatancy.

Although the clay contents are a main factor in causing thixotropy of this quicksand, another point must not be neglected. Its average particle size is distinctly smaller than that of the ordinary sand. Table I. gives a classification according to particle sizes, as determined by a set of sieves (percentages). The columns correspond to the figures of the samples mentioned above.

The quicksand of Knott End (column I) is outstanding as being fairly homogeneous and having a large majority of particles smaller than the finest sieve used, 87 per cent. having a diameter below $130\mu$. The greater part of these small particles had a velocity of sedimentation of

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TABLE I.

| Diameter of grains in $\mu$. | 1. | 2. | 3. | 4. | 5. | 6. |
|---|---|---|---|---|---|---|
| Less than 130 (passes through sieve 1) | 87 | 39·4 | 16·6 | 0·51 | 1·8 | 0·4 |
| Between 130 and 210 (residue on sieve 1) | 7·9 | 29·6 | 60·2 | 4·8 | 6·4 | 2·2 |
| Between 210 and 280 (residue on sieve 2) | 0·8 | 21·6 | 19·8 | 17·7 | 9·1 | 9·9 |
| Between 280 and 420 (residue on sieve 3) | 3·2 | 9·4 | 3·0 | 73·5 | 73·5 | 60·4 |
| Between 420 and 850 (residue on sieve 4) | 0·9 | — | 0·3 | 1·8 | 8·3 | 24·1 |
| Over 850 (residue on sieve 5) | — | — | 0·1 | 1·7 | 0·9 | 3·0 |

Sieve 1 with 200 meshes per inch; 2 with 120; 3 with 90; 4 with 60; 5 with 30 meshes per inch.

about 0·175 cm. sec.$^{-1}$, *i.e.*, the diameter was about 50$\mu$; a smaller, but appreciable percentage had a velocity of sedimentation of 0·07 cm. sec.$^{-1}$, *i.e.*, the diameter was about 30$\mu$. Ordinary sand from Knott End (column 2) was also finely grained, but the particle sizes were more equally distributed over a larger range of diameters. The high degree of dispersion of this quicksand perhaps also favours its thixotropy, in so far, as a comparatively small amount of clay is able to maintain a looser packing. On the other hand, the particles are still sufficiently large to cause dilatancy, if the clay is not moist enough. If a very finely powdered quartz (diameter about 1$\mu$) is mixed with the clay, even in a marked excess, dilatancy disappears entirely.

In the case of this quicksand we are dealing with a phenomenon which is obviously identical with one well known in ceramics : a poorly plastic mass is made plastic (in our case also thixotropic) by adding a certain small amount of a strongly plastic substance.

The correlation between thixotropic behaviour and loose packing on the one side, dilatancy and close packing on the other, was as strong as ever.[4] As an indication of the kind of packing, the volume of sedimentation was used again, it being large in the case of loose packing, small

TABLE II.—AMOUNT OF SOLID SUBSTANCE 3 g. ; AMOUNT OF LIQUID (SEA WATER) 6 c.c.

| Solid Substance. | Heights of | | Heights of Sediment (Calculated for a Height of 10 cm. of the Liquid Column). |
|---|---|---|---|
| | Liquid Column (Observed). | Sediment (cm.) (Observed). | |
| Quicksand (Knott End, Fleetwood) | 10·5 | 3·8 | 3·6 |
| Ordinary sand (Knott End, Fleetwood) | 10·0 | 3·0 | 3·0 |
| Fine particles of the quicksand (clay, etc. ; diameter below 5$\mu$) | 10·9 | 5·8 | 5·3 |
| Residue of quicksand (coarse particles) | 10·9 | 3·5 | 3·2 |
| Residue of quicksand + fine particles | 10·7 | 3·9 | 3·65 |

in that of close packing. The sedimentation volume was determined by allowing the sand to settle in test-tubes, having the same diameter of about 1 cm.; the volume was determined after 24 hours. Table II. shows that both the ordinary sand and the residue of the quicksand after separation from the clay, have practically the same small volume of sedimentation of about 3·0. That of the natural quicksand is markedly higher, 3·6, whilst that of the clay separated from the particles, is very much higher, 5·3.

Table III. shows further that the volume of sedimentation of ordinary sand in pure water and in sea water is practically the same. We are apparently dealing in both cases with close packing due to the fairly large size of the particles and, consequently, the electric charge does not exert a marked influence. In previous experiments with a very fine quartz powder (a high percentage of the particles having diameters between 1 and 10μ) close packing was found only in pure water.

TABLE III.—AMOUNT OF SOLID SUBSTANCE 3 g.; AMOUNT OF LIQUID 6 c.c.

| Solid Substance. | Liquid. | Heights of | | Heights of Sediment (Calculated for a Height of 10 cm. of the Liquid Column). |
| | | Liquid Column (Observed). | Sediment (cm.) (Observed). | |
|---|---|---|---|---|
| Ordinary sand . . (New Brighton) | pure water | 10·3 | 2·9 | 2·8 |
| Ordinary sand . . (New Brighton) | sea water | 10·6 | 3·0 | 2·8 |
| Finely powdered quartz . | pure water | 11 | 3·3 | 3·0 |
| Finely powdered quartz . | sea water | 11 | 4·8 | 4·3 |

There the volume of sedimentation was 3·0, a value agreeing fairly well with those obtained with ordinary sand.

The samples of quicksand from Southport and New Brighton were not thixotropic. It is not yet possible to say whether the mobile state within their natural surroundings is really caused by other factors, as mentioned above, or whether perhaps the samples were collected in a way which did not suit our purpose. For it is obvious that, if the thixo-tropy of a quicksand is caused by the presence of fine clay, the latter may be washed out on the surface, and therefore the samples ought to be taken

TABLE IV.—AMOUNT OF SOLID SUBSTANCE 3 g.; AMOUNT OF LIQUID (SEA WATER) 6 c.c.

| Solid Substance. | Heights of | | Heights of Sediment (Calculated for a Height of 10 cm. of the Liquid Column). |
| | Liquid Column (Observed). | Sediment (cm.) (Observed). | |
|---|---|---|---|
| Quicksand . . . (Southport) | 10·3 | 3·2 | 3·1 |
| Ordinary sand . . (Southport) | 10·4 | 3·0 | 2·9 |
| Quicksand . . . (New Brighton) | 10·6 | 3·1 | 2·9 |
| Ordinary sand . . (New Brighton) | 10·6 | 3·1 | 2·9 |

from somewhat deeper layers. The sedimentation volumes recorded in Table IV. seem to indicate, that for the quicksand of Southport the packing is looser than that of the ordinary sand, *i.e.*, there might be a tendency to show thixotropic behaviour. In this case the quicksand also contained a certain amount of clay,—distinctly more than the ordinary sand, much less however than the amount found in the quicksand of Knott End.

In all these sands the size of the grains is larger than with both the sands from Knott End (cf. Table I.). The quicksand from Southport is distinctly finer grained than the other three sands.

This paper is only meant as a preliminary attack on this whole problem and makes an attempt to show that thixotropy comes into play in natural systems of this kind. A more thorough investigation would need the collaboration of a geologist, who could critically examine the occurrence of the quicksand, and devise trustworthy methods of collecting it.

## Summary.

1. A sample of quicksand from Knott End, Fleetwood, was distinctly thixotropic, in contrast to an ordinary sand taken from the neighbourhood.

2. The thixotropy of the quicksand is ascribed to the presence of 2·1 per cent. of a fine plastic clay, the ordinary sand containing only 0·3 per cent. When the clay—together with all particles having a diameter below 10$\mu$—was separated from the coarser grains, the residue was no longer thixotropic. On re-mixing the clay with the residue, thixotropic behaviour reappeared. An important further feature is that the particles of the quicksand were more homogeneous and smaller than those of the ordinary sand.

3. The correlation between thixotropy and loose packing (the latter being indicated by a large sedimentation volume) was always found to hold. All the non-thixotropic sands had a smaller volume of sedimentation, which was practically identical with that of a closely packed fine quartz powder in pure water.

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# ON THE THEORY OF THE COAGULATION OF COLLOIDS AND OF SMOKES: AN AMENDMENT.

By W. R. Harper.

In an earlier communication[1] the author has discussed the experimental evidence in support of the formula of Smoluchowski for the coagulation of smokes and the rapid coagulation of colloids, concluding that there was good reason for believing the formula to give too high

[1] *Trans. Faraday Soc.*, 1934, **30**, 636.

a value for the coagulation coefficient, and suggesting that the observed values should be accounted for by a departure of the particles used from a perfectly spherical form. Reasons were given for rejecting the mathematical treatment used by Smoluchowski in deriving his formula, and an alternative formula was calculated from some earlier work of the author's on the recombination of gaseous ions. The proposed coagulation coefficient was one quarter of that of Smoluchowski. Though differing from his in the right direction, the new coagulation coefficient seemed to be *too small* to be easily reconcilable with the experiments. It was thought possible that the approximations in the calculations might in part be responsible for the low value, though a comparison of the theoretical and observed recombination coefficients in air at high pressure made it more probable that the error was in the opposite direction. The explanation has now been traced to a numerical mistake in the earlier paper on which the coagulation theory was based. For the discovery of this mistake the author is indebted to Dr. F. J. W. Whipple. After correction, the revised coagulation coefficient is three-quarters of that of Smoluchowski, a value which seems to the author to be now quite compatible with the experimental results if the particles were non-spherical even if the indication that it is still too high a value should prove correct. Incidentally, this indication is now strengthened.

The corrections to the theory of recombination are being presented elsewhere.[2] They lead to the formula $3\pi n_1 n_2 \sigma (D_1 + D_2)$ for the collision frequency, instead of $\pi n_1 n_2 \sigma (D_1 + D_2)$ as shown on page 629 of the earlier paper, so that $\frac{1}{2}\chi$ becomes $3\pi\sigma D$ instead of $\pi\sigma D$—as against Smoluchowski's $4\pi\sigma D$.

The factor on page 641 of the earlier paper by which the collision frequency is increased by mutual electrostatic attraction is unchanged except that the numerical value of $\sigma_0$ occurring in it should be $b'b'' \times 2 \cdot 03 \times 10^{-6} \times 273/\theta$ cm.

The generalised value of $\frac{1}{2}\chi$ on page 642 becomes

$$6\pi a_0 D[1 - \exp\{-a_0/\lambda_0\}],$$

and the generalisation is of importance when $a_0/\lambda_0 < 6$.

$a_0/\lambda_0$ for a gas should have been given on page 642 as

$$\frac{3\lambda'\sqrt{m_0\rho'N(\theta)}}{2\rho_0 a_0(1 + \lambda'/a_0)},$$

where $N(\theta)$ is the number of molecules per c.c. of a perfect gas at temperature $\theta$ and 760 mms. pressure, since $u$ in the formula for $\mu$ should have been dashed to refer to the gas molecule. In consequence, some slight modifications are required in the subsequent conclusions. For smoke particles of radius $10^{-6}$ cms. the correction to the collision frequency amounts to 60 per cent. not 20 per cent. For very small smoke particles the factor which counteracts the Cunningham factor is $a_0/\lambda_0$ (as above), and the residue is $3\lambda'\sqrt{m_0\rho'N(\theta)}/2\rho_0 a_0$. For stearic acid particles of radius $10^{-7}$ cms. its value is $1\frac{1}{2}$, so the Cunningham factor is nearly nullified. *Very* small homogeneous particles should therefore coagulate at about the same rate as large particles, unless, as is probable, they do not always coagulate on colliding.

The discussion requires no further modification.

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[2] *Phil. Mag.*, in the Press.

# A FURTHER NOTE ON THE DIFFUSION OF VOLATILE MATERIALS INTO AN INERT GAS STREAM.

By ERIC PRESTON.

In a previous communication[1] it was shown that the evaporation of the metallic oxide vapours of PbO, $K_2O$ and $Na_2O$, from the surface of molten glasses into a stream of nitrogen took place in a manner according to the equation of D. Enskog.[2] The data for this conclusion were obtained from dynamic determinations of the vapour pressures of these oxides, the experimental procedure for which has been described elsewhere.[3] Considerations of the Herz-Knudsen equation in conjunction with the degree of saturation of volatile material in the inert gas stream demonstrated that the unknown relationship existing between these two quantities approximated to the form of the Enskog equation.

The Herz-Knudsen equation was assumed to give a figure proportional to the number of molecules impacting upon unit area of the wall of the gas stream, and, in the light of the Enskog equation, the diffusion of these molecules into the gas stream in the attempt to establish their partial pressure, showed that volatilisation or evaporation under the conditions of these experiments was in essence a process by which material diffused into the surrounding atmosphere from a thin " super-surface " layer, of molecular dimensions in equilibrium with the liquid phase according to the Herz-Knudsen equation. It is interesting to note that M. Zentnerszwer, C. Wekerovna and Z. Majevska[4] have arrived at a similar conclusion by studies of the evaporation of water, benzol and toluol in an air stream, which process they found to be purely physical and determined by the diffusion from a saturated layer in contact with the liquid. No chemical equilibrium such as liquidogenic ⇌ gasogenic molecules was involved.

Further researches on the volatilisation of lithium oxide from lithia-silica glasses[5] have permitted the comparison between the experimental results and the Enskog equation to be carried a stage further, but not, unfortunately, to completion.

## Theoretical Discussion.

The Enskog equation for the interdiffusion of two gases of molecular weights $M$ and $M'$ is given to a first approximation by,

$$D, \text{ the diffusion coefficient} = \frac{3\sqrt{RT}}{32\sqrt{2\pi}N_A\psi}\sqrt{\frac{M + M'}{MM'}}\frac{1}{c + c'},$$

in which $c$ and $c'$ are the respective concentrations of the two gases, and $\psi$ depends on the law of force between molecules.

[1] E. Preston, *Trans. Faraday Soc.*, 1933, **29**, 1188.
[2] *Physikal Z.*, 1911, **12**, 533.
[3] E. Preston and W. E. S. Turner, *J. Soc. Glass Tech.*, 1932, **16**, 219.
[4] *Bull. Acad. Polonaise*, 1932, A, 369.
[5] E. Preston and W. E. S. Turner, *J. Soc. Glass Tech.*, 1934, **18**, 143.

It is assumed for the purposes of the present note that $\psi$ is constant for all materials, for Graham's law of diffusion may be considered as a special case in the application of the Enskog equation. Applying the above equation, and considering the gases to be diffusing into themselves we have, $M = M'$, $c = c'$ and is constant for all gases at constant temperature and pressure, then,

$$D = K\sqrt{\frac{2M}{M^2}}\frac{1}{C}, \quad i.e. \quad D \propto \frac{1}{\sqrt{M}}.$$

Graham's law is known to hold to a fair degree of accuracy for many gases, and hence we may conclude that $\psi$ does not sensibly differ from one material to another. It may be of a highly complex form, but we are only concerned with its numerical value when inserted in the Enskog equation. For perfectly elastic spheres,

$$\psi = \frac{(d + d')^2}{16}.$$

We may now write the equation in the form,

$$D = K\sqrt{\frac{M + M'}{MM'}}\frac{1}{c + c'}.$$

Previously it was shown that in the case of the volatilisation at $1200°$ of the materials $K_2O$, $Na_2O$ and PbO, then, ignoring the factor $\sqrt{\dfrac{M + M'}{MM'}}$, the degree of saturation of the volatile materials in the issuing gas stream was given approximately by an equation of the type,

$$\text{Degree of saturation for a constant rate of flow} = \frac{a}{a + y},$$

in which $y$ was proportional to the number of volatilising molecules impacting in unit time on unit area of the wall of the gas stream, and was derived from the Herz-Knudsen equation in which $m$, the ideal rate of evaporation *in vacuo*, is given by

$$m = p\sqrt{\frac{M}{2\pi RT}}.$$

The value $\dfrac{p}{\sqrt{MT}}$ was designated the " $H$-$K$ " number and was assumed to be a measure of the concentration, $c'$, of the volatilising molecules.

It is now shown by the study of the lithia-silica glasses that the factor $\sqrt{\dfrac{M + M'}{MM'}}$ can also be accounted for, bringing the agreement with the Enskog equation a little closer.

The method of the dynamic determinations of the vapour pressures [6]

[6] Apparently originally due to H. von Wartenberg, *Z. Elektrochem.*, 1913, **19**, 482 ; *Z. anorg. Chem.*, 1912, **79**, 76, this method has been used by D. D. Jackson and J. J. Morgan, *J. Ind. Eng. Chem.*, 1921, **13**, 111 and 225, in the study of the volatilities of various potash compounds. Jackson and Morgan point out the limitation of the method to vapour pressures under 25 or 30 mm. Hg, on account of back diffusion and the difficulty of working with high rates of gas flow. They place the accuracy of the method at $\pm$ 10 per cent. It seems probable to the writer that the critical minimum rate of flow below which back diffusion occurs is first a function of the dimensions of the apparatus, and secondly of the partial pressures to be measured.

assumes a linear relationship between the rate of inert gas flow and the degree of saturation attained, and the true vapour pressure is determined by extrapolation to zero rate of flow. More will be said about this subsequently. Fig. I, reproduces typical results for determinations made on two lithia-silica glasses at 1300°. The whole of the results presented in this paper refer to this temperature, for the volatile oxides PbO, $K_2O$, $Na_2O$ and $Li_2O$.

The previous publication and the present note attempt to show that there is some relation between the Herz-Knudsen equation and evaporation under normal conditions and the diffusion of gases on the basis of the Enskog equation. It may be noted that I. Langmuir and D. B. Langmuir [7] have concluded that under their conditions of experiment " the resistance to evaporation from a pure water surface may be looked upon as a resistance to diffusion through a layer of relatively quiet air."
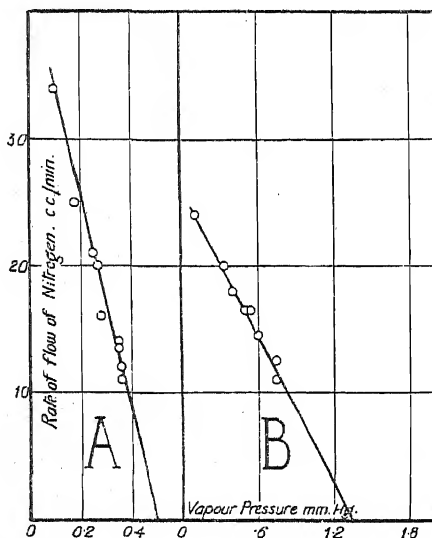


They found also that in the evaporation of ether, wind velocities of from 0 to 152 cm./sec. only served to increase the rate of evaporation by a factor of approximately three. In contradistinction to this, G. Hedestrand [8] had previously concluded that the rate of evaporation for a given material was proportional to the vapour pressure. Now under certain conditions of experiment this statement can accurately represent the results obtained, for Professor W. E. S. Turner and the present writer have observed that in the evaporation of potassium oxide from a series of pure potash-silica glasses when heated in a still atmosphere in a furnace tube the volume of which (670 c.c.) was large compared to the area of the evaporating surface (about 5 s.cm.), the rate of evaporation was practically directly proportional to the vapour pressure of $K_2O$ above the glass surface. This is shown in Table I., and similar results have been obtained for soda-silica and lithia-silica glasses. In fact, the general form of the volatilisation-temperature relationships for all the glasses was

FIG. I.—Vapour Pressures at 1300° C. for Two Lithia-Silica Glasses.

A, 38·22 per cent. $Li_2O$. B, 50·09 per cent. $Li_2O$.

$$\log r = A - \frac{B}{T_{Abs}},$$

in which $r$ was the initial rate of volatilisation and $A$, and $B$, were constants for each particular glass.

[7] J. Physic. Chem., 1927, **31**, 1719.          [8] Ibid., 1924, **28**, 1245.

TABLE I.—Comparison of Vapour Pressures and Initial Rates of Volatilisation for the $K_2O$-$SiO_2$ Glasses.

(1) 49·83 per cent. $K_2O$.      (2) 43·46 per cent. $K_2O$.

| Temp. °C. | Vapour Pressure, mm. Hg. | | Initial Rate of Volatilisation, mg./cm.²/20 Hrs. | | Ratios. | |
|---|---|---|---|---|---|---|
| | $p_1$. | $p_2$. | $x_1$. | $x_2$. | $\dfrac{x_1}{x_2}$. | $\dfrac{p_1}{p_2}$. |
| 1400 | — | — | 118·0 | 62·0 | 1·90 | — |
| 1300 | 3·10 | 1·82 | 54·8 | 31·0 | 1·77 | 1·71 |
| 1250 | 2·10 | 1·25 | — | — | — | 1·68 |
| 1200 | 1·48 | 0·80 | 26·8 | 13·8 | 1·94 | 1·85 |
| 1150 | 0·90 | 0·50 | — | — | — | 1·80 |
| 1100 | — | — | 11·7 | 6·6 | 1·77 | — |
| | | | Average values of ratios | | 1·87 | 1·76 |

## Experimental Results.

It is pertinent to enquire what fraction of the ideal rate of evaporation is obtained in isothermal heatings carried out at normal pressures. We should not expect this fraction to be the same for all materials. Table II. gives the results for the volatilisation of the alkaline oxides conducted under precisely similar conditions for each glass at 1300°.

TABLE II.—The Percentage of the Ideal Rate of Evaporation Obtained at Normal Pressures.

| Glass. | Initial Rate of Volatilisation at 1300°, mg./cm.²/20 Hrs. | Vapour Pressure at 1300°, mm. Hg. | Percentage of "Ideal Rate," (gm./cm.²/sec.). |
|---|---|---|---|
| $Li_2O$-$SiO_2$ | | | |
| 50·09 % $Li_2O$ | 46·0 | 1·35 | 0·0059 |
| 38·22 ,,  ,, | 17·0 | 0·50 | ·0058 |
| $Na_2O$-$SiO_2$ | | | |
| 48·85 % $Na_2O$ | 20·0 | 1·37 | 0·0017 |
| 44·58 ,,  ,, | 13·0 | 0·85 | ·0018 |
| $K_2O$-$SiO_2$ | | | |
| 49·32 % $K_2O$ | 54·8 | 3·10 | 0·0017 |
| 43·46 ,,  ,, | 31·0 | 1·82 | ·0018 |

The agreement in the values of the percentage of the ideal rate of evaporation for $Na_2O$ and $K_2O$ may be quite fortuitous, since an accuracy greater than $\pm$ 10 per cent. is not claimed for the vapour pressure values. Nevertheless, it is interesting to note that for the heavier molecules $Na_2O$ and $K_2O$ the percentage of the ideal rate of evaporation is roughly one-third of that for the $Li_2O$ molecules ($= 30$) which have very nearly the same mass as the nitrogen molecule ($N_2 = 28$), and the oxygen molecule ($O_2 = 32$). A further point of interest, and a somewhat remarkable fact, is that Hedestrand[8] in his experiments on the evaporation of water at room temperatures and normal pressures only obtained a rate of evaporation of 0·0023 per cent. of the ideal rate. The similarity

27 *

of this figure and the present values, which, although obtained at high temperatures, were at approximately 760 mm. pressure, is indeed striking and is indicative of the effect of external pressure on the rate of evaporation. Further research in this direction undoubtedly lies in studies of the rates of evaporation at reduced pressures. It is possible that the law of the effect of pressure may be found to be, again, a hyperbolic one.

For a glass containing 30 per cent. of PbO the percentage of the ideal rate of evaporation at 1300° was 0·0028, but this value is based on the assumption that the loss at this temperature was entirely due to lead oxide, which was not strictly so, for the glass contained small quantities of $Na_2O$ and $K_2O$. The loss of these constituents, however, was certainly less than 10 per cent. of the whole, 113 mg./cm.$^2$/20 hours.

The writer believes that an explanation for the apparently anomalous behaviour of the lithium oxide-silica glasses lies in the fact that in the $Na_2O$ and $K_2O$ glasses there is strong evidence for the belief that the alkaline constituent is volatilising chiefly from the compounds $Na_2O \cdot SiO_2$ and $K_2O \cdot SiO_2$ respectively, but from the lithium oxide

TABLE III.—RESULTS OF VAPOUR PRESSURE DETERMINATIONS OF THE VOLATILE CONSTITUENTS OF SEVERAL GLASSES AT 1300° C.

| Rate of Flow ($N_2$), cc./min. | Determined Vapour Pressure, mm. Hg. | Degree of Saturation, $p_r/p_0$. | " H-K " Number. | $\sqrt{\dfrac{M + M'}{MM'}}$. |
|---|---|---|---|---|
| *Lead Oxide*   30 % *PbO Glass.* | | | | |
| 0 | 2·55 | — | | |
| 10 | 1·90 | 0·745 | | |
| 15 | 1·60 | 0·627 | 0·171 | 0·201 |
| 20 | 1·25 | 0·490 | | |
| *Sodium Oxide.*   48·85 % $Na_2O$ *Glass.* | | | | |
| 0 | 1·36 | — | | |
| 10 | 0·95 | 0·698 | | |
| 15 | 0·75 | 0·551 | 0·173 | 0·227 |
| 20 | 0·55 | 0·405 | | |
| *Potassium Oxide.*   49·32 % $K_2O$ *Glass.* | | | | |
| 0 | 3·15 | — | | |
| 10 | 1·95 | 0·619 | | |
| 15 | 1·35 | 0·428 | 0·325 | 0·215 |
| 20 | 0·75 | 0·238 | | |
| *Lithium Oxide.*   38·22 % $Li_2O$ *Glass.* | | | | |
| 0 | 0·50 | — | | |
| 10 | 0·39 | 0·780 | | |
| 15 | 0·335 | 0·670 | 0·091 | 0·262 |
| 20 | 0·27 | 0·540 | | |
| *Lithium Oxide.*   50·09 % $Li_2O$ *Glass* | | | | |
| 0 | 1·35 | — | | |
| 10 | 0·82 | 0·607 | | |
| 15 | 0·57 | 0·422 | 0·246 | 0·262 |
| 20 | 0·32 | 0·237 | | |

glasses, chiefly from the compound $2Li_2O \cdot SiO_2$.[9] That is, the state of chemical combination exerts an influence upon the volatilisation under such conditions, an influence which is only similar in the case of similar combination. Or, further, in such volatilisation from liquid solution the " accommodation coefficient " [10]

$$\alpha = e^{-\frac{M\mu_0^2}{2RT}}$$

is dependent on the energy required to release the volatile component from combination and which we may assume to be proportional to $\frac{M\mu_0^2}{2}$ in which $\mu_0$ is the minimum velocity which the molecules must possess to be removed from the liquid surface.

Table III. gives a summary of the results of dynamic determinations of the vapour pressures of the glasses of stated compositions. The degree of saturation is simply $p_r/p_0$ where $p_r$ is the observed partial pressure of volatile material at a rate of nitrogen flow, $r$, and $p_0$ the extra-
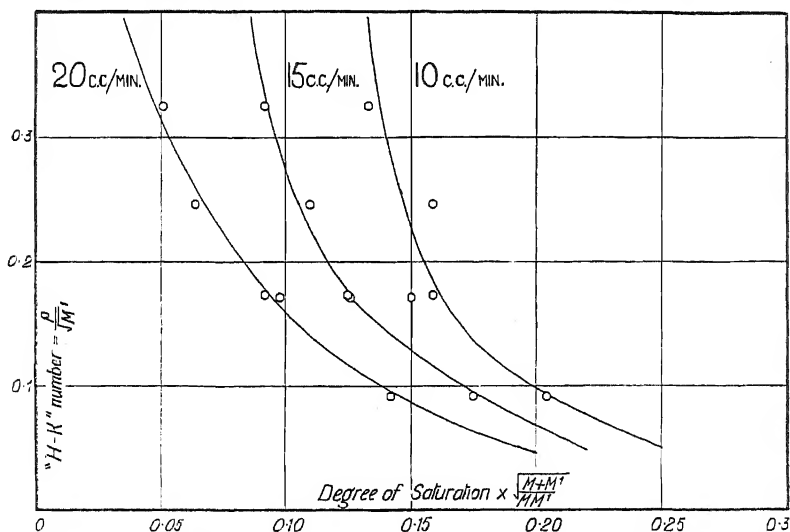


FIG. 2.—Relation between "H.K." number and the Degree of Saturation for the fine glasses at 1300°.

polated value of the vapour pressure at zero rate of flow. The " $H\text{-}K$ " number is $p_0/\sqrt{M}$. On plotting degree of saturation against " $H\text{-}K$ " number, no simple relationship is apparent as was the case in the previous communication, but if the degree of saturation be multiplied by the factor $\sqrt{\dfrac{M + M'}{MM'}}$ for each of the five glasses, as is done in Fig. 2, then a hyperbolic relationship is seen to fit the results quite well, irrespective of molecular type. From Fig. 3 the relationship for a given rate

[9] See the series of papers by E. Preston and W. E. S. Turner, *J. Soc. Glass Tech.*, previously quoted; also E. Preston and W. E. S. Turner, *J. Amer. Ceram. Soc.*, 1934, **17**, 26.
[10] As defined by S. Myamoto, *Trans. Faraday Soc.*, 1933, **29**, 794.

of flow is seen to be of the type

$$\text{`` }H\text{-}K\text{ '' number} = \frac{a}{\text{Degree of Saturation }\sqrt{\dfrac{M + M'}{MM'}}} + b.$$

Expressing this in the form of the Enskog equation, we have

Degree of Saturation

$$\times \left(\frac{M + M'}{MM'}\right) = a \times \sqrt{\frac{M + M'}{MM'}} \times \frac{1}{b + (\text{`` }H\text{-}K\text{ '' Number})},$$

in which $a$ and $b$ are constants.

From which we are led to assume that D, the diffusion coefficient for different materials, is given by an expression—

$$D \text{ (the diffusion coefficient)} = K \times \text{Degree of Saturation} \times \left(\frac{M + M'}{MM'}\right),$$
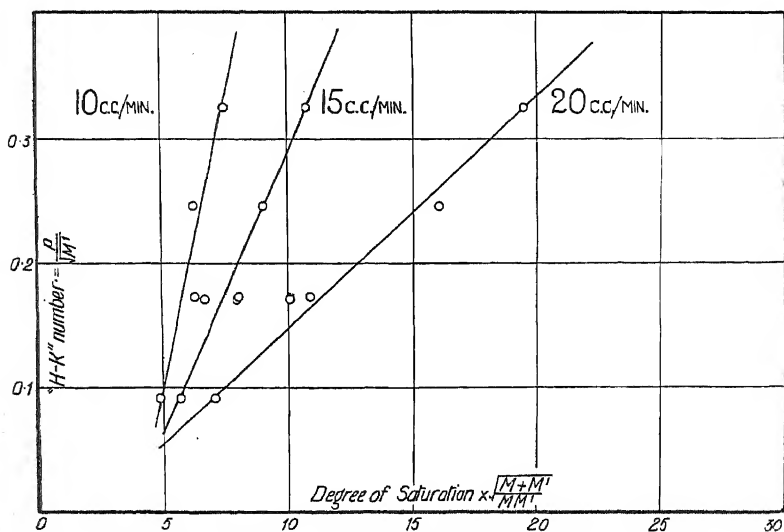


FIG. 3.—Relation between " H.K." number and the Degree of Saturation.

for the same rate of flow of nitrogen (the constant $b$) and the same number of impacting molecules ("$H$-$K$" number). This is capable of some degree of verification in the particular case of the $Na_2O$ and $PbO$ containing glasses, which fortunately have the same calculated "$H$-$K$" number at $1300°$ C. From the previous equation we have :—

Diffusion Coefficient, $D_{PbO} = K \times$ Degree of Saturation

$$\text{at given rate of flow of N}_2 \times \frac{M_{N_2} + M_{PbO}}{M_{N_2} \times M_{PbO}}$$

and similarly for $Na_2O$.

These results have been calculated and are tabulated in Table IV.

Now from the Enskog equation, for constant nitrogen flow, and constant number of diffusing molecules, we should have

$$D_{Na_2O}/D_{PbO} = \sqrt{\frac{M_{N_2} + M_{Na_2O}}{M_{N_2} \times M_{Na_2O}}} \times \sqrt{\frac{M_{N_2} \times M_{PbO}}{M_{N_2} + M_{PbO}}}$$

$$= \frac{0.227}{0.201} = 1.130.$$

This ratio is very nearly the same as the experimentally determined ratios in Table IV. In the later section some explanation is advanced for the progressive increase in $D_{Na_2O}/D_{PbO}$ as determined experimentally.

**Evaporation in a Still Atmosphere at Normal Pressure.**

It is possible to utilise the results showing the fraction

TABLE IV.

| Rate of $N_2$ Flow. c.c./min. | (Diffusion Coefficient)/$K$. | | Ratios, $\dfrac{D_{Na_2O}}{D_{PbO}}$. |
|---|---|---|---|
| | PbO. | Na₂O. | |
| 20 | 0·01960 | 0·02035 | 1·050 |
| 15 | 0·02508 | 0·02765 | 1·100 |
| 10 | 0·02980 | 0·03500 | 1·175 |

of the ideal rate of evaporation and to demonstrate that this is a semi-fundamental quantity. That is, at a given pressure, a certain rate of evaporation cannot be exceeded, just as in absolute vacuo we cannot exceed the ideal rate of evaporation.

By evaporation into a still atmosphere is meant evaporation such as that carried out at high temperatures of the alkaline oxides from molten glasses [5] in which there is no appreciable air current over the evaporating surface. If the fraction of the ideal rate of evaporation be then found it is possible to estimate the heat of

TABLE V.—ESTIMATED MINIMUM VELOCITIES OF THE EVAPORATING MOLECULES AT 1300° C., 760 MM. Hg.

| Oxide. | Fraction of Ideal Rate. | $\mu_0$, Min. Molecular Vel. |
|---|---|---|
| Li₂O | $5 \cdot 9 \times 10^{-4}$ | $30 \times 10^4$ cms./sec. |
| Na₂O | $1 \cdot 7 \times 10^{-4}$ | $21 \times 10^4$ ,, |
| K₂O | $1 \cdot 8 \times 10^{-4}$ | $17 \times 10^4$ ,, |

evaporation of the material and the energy which the molecules must possess to leave the liquid surface.

The accommodation coefficient or fraction evaporated is given by [11]

$$\alpha = e^{-\frac{M\mu_0^2}{2RT}}.$$

We may therefore estimate $\mu_0$ in the case of the three alkaline oxides Li₂O, Na₂O and K₂O, and this is shown in Table V.

Further, if we write the equation in the usual manner,

$$\alpha = e^{-\frac{E}{RT}},$$

we get for the energies E, of the three alkaline oxides the above results.

TABLE VI.

| Oxide. | 1300° C, 760 mm. Hg, $E$. | Previously Reported Values for Heat of Evaporation (Preston and Turner). |
|---|---|---|
| Li₂O | 30,630 cals. | −34,700 cals. |
| Na₂O | 33,000 ,, | −38,000 ,, |
| K₂O | 34,500 ,, | −37,000 ,, |

In the last column of the foregoing Table are given the heats of evaporation as calculated from the usual vapour pressure results by the

[11] From Maxwell's distribution law of the components of velocities in a given direction, *i.e.*, at right angles to the liquid surface.

Nernst equation. It is readily seen that the use of the fraction of the ideal rate of evaporation in the equation—

$$\text{Fraction of ideal rate} = e^{-\frac{E}{RT}},$$

gives a result for $E$ in close agreement with the heat of evaporation of the volatilising material.

It is interesting to compare these results with calculations from the results of other workers on the evaporation of water. In no case was the evaporation conducted in a *still* atmosphere, all workers using an air flow method, but the lower the air flow the more nearly does the calculated energy approach the accepted value of 538 cals./gm. for the heat of vaporisation.

TABLE VII.

| Worker. | Temperature, Per Cent. | Fraction of Ideal Rate of Evaporation. | Min. Molecular Velocity. $\mu_0$. | $E$, cals. per gm. |
|---|---|---|---|---|
| Hedestrand . | 20 | $2 \cdot 3 \times 10^{-5}$ | $17 \times 10^4$ cm./sec. | 350 |
| Adam . . | 18 | $4 \cdot 5 \times 10^{-7}$ | $20 \times 10^4$ ,, | 476 |
| Rideal . | 25 under reduced pressure 24 mm. Hg. | $4 \cdot 2 \times 10^{-3}$ | $12 \times 10^4$ ,, | — |

It may be noted that when the fraction of the ideal rate of evaporation is of the same order as that for $Na_2O$ and $K_2O$ then the minimum velocity which the molecules must possess is also approximately the same. The average velocities of water vapour molecules at $0°$ C and 760 mm. Hg are given as $7 \cdot 08 \times 10^4$ cm./sec.[12] So we may say that evaporation at normal pressure is effected by those molecules leaving the liquid surface with individual velocities in the direction of evaporation (*i.e.* at right angles to the surface) approximately three times greater than the average velocities of the same molecules in the gaseous condition at that temperature.

## The Degree of Saturation and the Rate of Inert Gas Flow.

The writer believes that the relation between the degree of saturation and the rate of inert gas flow over an evaporating surface is not linear as represented, but is given by the hyperbolic form of curve shown dotted in Fig. 4 ; for whatever the rate of nitrogen flow, some evaporated molecules will be removed in the gas stream.

This would tend to rectify the low values of $D'/D''$ found in an earlier section, and to bring them to a more constant value. It would also explain the results of M. Zentnerszwer, C. Wekerovna and Z. Majewska,[4] who found that the velocity of evaporation of $H_2O$, benzene and toluol was directly proportional to the rate of air flow over the surface up to a limiting value of the velocity of evaporation beyond which the cooling effect exerted a pronounced influence. It appears that these workers' results were on that part of the curve parallel to the vertical axis, for their results would give a constant degree of saturation.

[12] *Physical Tables,* J. B. Clark, 12th Ed. Oliver and Boyd.

Two factors tend to set the experimental results on a straight line as shown in Fig. 4, in the apparatus used by the writer.  Firstly, at low rates of $N_2$ flow, back diffusion would tend to give slightly higher results for the calculated vapour pressure, and secondly, at higher rates of flow the cooling effect of the gas stream would tend to give a low result for the partial pressure.  Then, over a narrow range, the experimental determinations may form a good straight line which is not greatly in error when extrapolated to zero rate of flow to give the true vapour pressure.

## Conclusions.

Further evidence is advanced for the view that evaporation or volatilisation proceeds from a " super surface " layer in equilibrium with the liquid phase in accordance with the Herz-Knudsen equation, and that its removal is governed by gaseous diffusion into the surrounding atmosphere.



Fig. 4.—Probable True Relationship (shown dotted) between Observed Partial Pressure and Rate of Inert Gas Flow.

The fraction of the ideal rate of evaporation is constant under constant conditions, and fundamentally dependent upon the external pressure.  At normal pressures a consideration of this fraction leads to the view that the molecular velocities of molecules leaving the liquid surface are about three times greater than the average velocity of the molecules in the normal gaseous condition, and further that the total energy of such molecules at the moment of leaving the liquid surface is approximately equal to the heat of vaporisation of the material.

It has been shown how the diffusion coefficient of the Enskog equation may be regarded as a function of the degree of saturation of the diffusing material in the gas stream, and the probable true relationship indicated between the determined partial pressure and the velocity of the gas stream.

In conclusion, the writer desires to express again his grateful thanks to Professor W. E. S. Turner of the Department of Glass Technology, Sheffield, for his continued interest in the work.

*The Department of Glass Technology,*
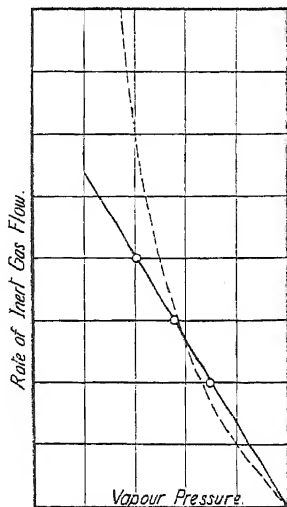         *The University,*
                 *Sheffield.*

# THE BLUE GLOW ON SURFACES AT −180° C. ATTRIBUTED TO NH OR NH₂ MOLECULES.

By R. Winstanley Lunt and J. E. Mills.

In the course of some experiments on the spectra emitted by electrical discharges in streaming ammonia,[1] some additional information has been obtained relating to the blue-green glow which appears when the gas drawn away from a discharge, but still containing some undecomposed ammonia, is cooled to the temperature of liquid air, and which was first reported by Lavin and Bates.[2]   These authors stated that with low gas pressures and high streaming velocities the glow could be obtained 1·5 metres away from the discharge zone ; they gave no details of the emission spectrum except that the 3360, 3370 NH bands were not to be observed.   The glow was not diminished when a catalyst for the destruction of atomic hydrogen was inserted in the gas stream, and no glow was to be seen when active nitrogen was passed over solid ammonia at − 180°. A 2-metre column of gas between the discharge and the vessel cooled to − 180° where the glow appeared showed no absorption for wave-lengths greater than 2000 Å.   It was concluded from these results that the glow could not be attributed either to atomic hydrogen or active nitrogen, and the suggestion was made that the molecule responsible for the emission was either NH or NH₂.   It was also reported that a blue glow was produced if oxygen was added to the gases drawn away from the discharge, and that under these conditions no luminescence could be obtained if the gases were subsequently cooled by a surface at − 180°.   When ethylene was used in place of oxygen a yellow glow appeared, and a white solid smelling intensely of cyanides could be condensed out from the gas stream at − 180°.

More recently Steiner and Dixon [3] sought for the luminescence described by Lavin and Bates ; they streamed ammonia through a high tension low frequency (50 cycle) alternating current arc over a range of flow speeds in the pressure range 0·07 to 1·00 mm. Hg., but were unable to detect any luminescence.   They observed a greenish-blue luminescence giving a continuous spectrum from yellow to blue when ammonia was added to active nitrogen and considered that it was identical with that observed in mixtures of oxygen and nitrogen after excitation by a discharge ; in support of this view they mention that the nitrogen they used contained appreciable amounts of oxygen.   A similar green luminescence had also been observed by Cario and Kaplan [4] when nitrogen containing small amounts of oxygen was passed through a discharge and then cooled to − 180°.   Since Steiner and Dixon were unable to obtain any luminescence from ammonia, they concluded that there was little if any evidence that the glow observed by Lavin and

[1] Lunt, Mills and Smith, *this vol.* p.  .
[2] Lavin and Bates, *Proc. Nat. Acad. Sci.*, 1930, **16**, 804.
[3] Steiner and Dixon, *Z. physik. Chem.*, B., 1932, **17**, 327.
[4] Cario and Kaplan, *Z. Physik*, 1929, **58**, 769.

Bates could be attributed to any fragment of the ammonia molecule drawn away from the discharge zone, and pointed out that a persistence of either NH or $NH_2$ molecules beyond the discharge zone was unlikely, since they could both disappear in exothermic bimolecular reactions. The small amounts of hydrazine formed in the discharge were thought to be in accordance with this view, since it was presumed that NH if present would react according to the equation

$$NH + NH_3 + M = N_2H_4 + M' \qquad . \qquad . \qquad . \quad (\text{I})$$
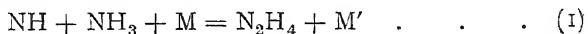
The actual yields of hydrazine indicated an NH partial pressure of the order of $10^{-5}$ mm. Hg. This significance attached to the low hydrazine yield is possibly incorrect, since Dixon and Steiner thought that appreciable amounts of atomic hydrogen were formed in the discharge used, and Dixon[5] has shown that hydrazine is readily destroyed by atomic hydrogen.

In further support of their views, they examined the spectrum of the gases drawn away from the low frequency discharge in an auxiliary weak high frequency discharge using external electrodes. In this spectrum the triplet NH bands at 3360, 3370 Å. were weak, whilst the second positive bands of nitrogen were strong; however, when the low frequency discharge was discontinued, the high frequency spectrum showed only the 3360, 3370 bands, and with much greater intensity than in the previous case. This result was taken to indicate that the likelihood of any NH molecules formed in the low frequency discharge being drawn away in the gas stream was very small.

It has now been found, in confirmation of the original claims of Lavin and Bates, that a blue surface luminescence may readily be produced when the gases issuing from a discharge in ammonia are cooled to − 180° C.; the glow could also be obtained from nitrogen-hydrogen mixtures.

The ammonia used in these experiments was purified by fractionation, drying over potash, barium oxide, and finally sodium. It was then refractionated. The nitrogen-hydrogen mixture (1 : 3) obtained from a cylinder was passed over potash, hot copper to remove the oxygen, then dried over phosphorus pentoxide and finally purified by passage through traps immersed in liquid air. No spectra associated with carbon or with oxygen were ever detected in these gases. Pressures were read on a McLeod gauge connected to the discharge tube by means of a tube freshly sputtered with gold to avoid the diffusion of mercury vapour.

A very intense glow was obtained, using an ozoniser discharge at pressures of the order of 1 mm. Hg; unfortunately, persistent stray discharges precluded the spectroscopic examination of the glow produced in this way. This difficulty was obviated by streaming ammonia under similar pressure conditions through an alternating current arc between water-cooled aluminium electrodes. There was no noticeable difference in the glow produced by 50 and 500 cycle excitation, and it was noticed that a high frequency discharge (ca. 500 kilocycles) between external electrodes was also effective. The glow obtained from mixtures of nitrogen and hydrogen was definitely weaker than from ammonia. On the other hand, no trace of the glow could be detected in streaming ammonia which had been intensely irradiated with the light from a condensed aluminium spark. In agreement with Lavin and Bates, no absorption could be detected, using a quartz spectroscope in a 2-metre column of the gases drawn away from a discharge in ammonia, nor was

[5] Dixon, *J.A.C.S.*, 1932, **54**, 4262.

any found in an oxoniser discharge in ammonia or nitrogen-hydrogen mixtures at pressures from 0·2 to 30 cm. Hg.

The spectrum of the blue glow on a surface cooled by liquid air was recorded with a six-hour exposure on a Raman spectrograph (Hilger type 413). The spectrum was found to consist solely of a broad band extending from about 5300 to 4400 Å., with a well-defined and approximately symmetrical intensity maximum at 5000 Å. The distribution of intensity suggests that the emission arises from a molecule decomposing on emission, the intensity maximum corresponding to an energy of 57 k. cals.

It was found that the addition of small quantities of palladium-diffused hydrogen in the region of the glow greatly enhanced the intensity. If sufficient hydrogen was admitted so that it diffused back against the ammonia stream into the discharge zone, there was no enhancement of the intensity of the glow, nor was any enhancement observable when hydrogen was mixed with ammonia before entering the discharge. The addition of nitrogen or ammonia in the region of the glow produced no effect, but oxygen, even in minute amounts, immediately quenched the glow. Through the kindly co-operation of Dr. E. J. B. Willey, experiments were also carried out in which ammonia was added to glowing active nitrogen at — 180° and at — 80°. No trace of the blue glow was discernible, neither was any change in the emission spectrum of the active nitrogen.

The fact that the glow was obtained in highly purified ammonia and in nitrogen-hydrogen mixtures confirms the view that the molecule responsible for the emission contains nitrogen and hydrogen only. Since the ammonia was only partly decomposed in passing through the discharge, it is clear that the surface at which the glow is seen at — 180° is one of solid ammonia. There is, however, no evidence that such a surface is essential to the development of the glow. The observation that minute amounts of oxygen introduced into the gas stream near the surface cooled to — 180° immediately quenched the glow is in agreement with the results of Lavin and Bates.

The failure of Steiner and Dixon to observe the glow is probably due to impurities in the ammonia used ; no precautions were taken to purify this gas, or, apparently, to exclude mercury vapour from the McLeod gauge used to measure the pressure in the discharge tube. In the experiments of Lavin and Bates and in those now reported, the ammonia was dried over sodium. Since Steiner and Dixon reported the presence of appreciable quantities of oxygen in the nitrogen they used, there appears to be little doubt that the glow they observed on adding ammonia to active nitrogen was identical with that described by Cario and Kaplan [4] arising in mixtures of nitrogen and oxygen. No great weight can be attached to the fact that Steiner and Dixon obtained a glow extending to the yellow that could readily be photographed, since it is difficult to make an exact comparison of the experimental details ; nevertheless, it does suggest that this glow is different from that we have observed.

The absence of the glow when active nitrogen is allowed to flow over a surface of solid ammonia at — 80° or at — 180°, in agreement with the experiments of Lavin and Bates, excludes a reaction between these substances from causing the glow. It does not, however, exclude a surface reaction between active nitrogen and NH, or $NH_2$ molecules. It appears to be very unlikely that active nitrogen is concerned in producing the glow because this can be obtained over a wide range of conditions

which differ considerably in their ability to produce active nitrogen, and in particular, under the conditions used most favourable to the production of active nitrogen, low frequency high current density discharges in nitrogen-hydrogen mixtures, the intensity of the glow was weak.

Since the photochemical decomposition of ammonia takes place almost exclusively according to the reaction [6]

$$NH_3 + h\nu = NH_2 + H$$
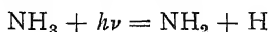
the failure to detect the glow using irradiated ammonia suggests that $NH_2$ is not the molecule concerned. It may be, however, that the amount of photochemical decomposition was insufficient; unfortunately, no measurements were made. Whatever may be the molecule responsible for the $\alpha$ band, the absence of this band from the spectrum of the exciting discharge also militates against the likelihood that this molecule, which is thought [7] to be $NH_2$, is concerned in the production of the blue glow.

One other point deserves mention : Steiner and Dixon observed that when the gases drawn away from (a) a low frequency discharge in ammonia (such as that used in connection with obtaining the spectrum of the glow) are subjected subsequently to (b) a weak high frequency discharge, the spectrum showed the $^3\Pi - {}^3\Sigma$ bands of NH very faintly, whilst using discharge (b) alone these bands are well developed. They interpreted this result as evidence against the persistence of NH molecules in the gas stream drawn from the discharge (a). These experimental results have now been confirmed, and it has also been observed that the diminution in intensity of the $^3\Pi - {}^3\Sigma$ NH bands when discharge (a) is used in addition to discharge (b) is rather more marked than that of the $^1\Pi - {}^1\Delta$ band at 3240 Å. It has also been found that the addition of a small amount of nitrogen (5 per cent.) to the ammonia stream results in an almost complete suppression of the NH bands when discharge (b) only is used. Steiner and Dixon's observation of a very low intensity of NH bands in discharge (b) when applied to the gases leaving discharge (a) is thus attributable to the nitrogen produced by discharge (a). Whatever may be the mechanism by which the NH bands are suppressed, there appears to be none by which molecular nitrogen could effect a transition of $^1\Delta$ NH molecules to the ground state.

The data now available show that atomic hydrogen and most probably also active nitrogen, are not concerned in the production of the glow. The enhancement of the glow by molecular hydrogen suggests that it arises from a reaction between some fragment of the ammonia molecule and molecular hydrogen on a surface of solid ammonia at $-180°$ C., and moreover since the glow can be obtained a considerable distance from the discharge zone, the fragment of the ammonia molecule concerned must be able to persist for an appreciable time. The only known metastable fragment of the ammonia molecule is the $^1\Delta$ state of NH; it was noticed that the $^1\Pi - {}^1\Delta$ NH band was well developed in the spectra of the discharge associated with the appearance of the glow. There is thus good reason to suppose that metastable $^1\Delta$ NH molecules will exist in the gases leaving the discharge zone, and that at the pressures used some would have survived for an appreciable time without reacting with themselves to give molecular hydrogen and nitrogen.

[6] Bonhoeffer and Harteck, *Grundlagen d. Photochemie*, Leipzig, 1933 ; Farkas and Harteck, *Z. physik. Chem.*, 1934, **27B**, 111.
[7] Rimmer, *Proc. Roy. Soc.*, 1923, **103A**, 696 ; Halthén and Nakamura, *Nature*, 1927, **119**, 235 ; Fowler and Badami, *Proc. Roy. Soc.*, 1932, **133A**, 325.

In discussing possible mechanisms for the production of the glow, it is necessary to review only those reactions in which the energy involved is in the neighbourhood of that corresponding to the long wave-length limit of the glow, 64,000 k. cals. Calculations of the energy evolved in the reaction

$$NH + {}^1\Sigma\, H_2 = NH_3 \qquad . \qquad . \qquad . \qquad (1)$$

depend on two quantities not accurately known, the heat of dissociation of ${}^3\Sigma$ NH, and the depth of this level below ${}^1\Delta$. Assuming 90 k. cals. for the former, and Mulliken's estimate [8] for the latter, 25 k. cals., the energy evolved in the above reaction is 87 k. cals. ; [9] allowing for uncertainties in the calculation, this is amply adequate to account for the glow. It is, however, difficult to conclude that the glow could be emitted by an excited ammonia molecule. The only two spectra associated with ammonia in the region 5100 Å. are the $\alpha$ band and the continuous spectrum noticed by Mitchell [10] when examining the continuous band at 3450 Å., excluding the vibration band at 5560 Å. observed in aqueous solution.[11] Mitchell came to the conclusion that the continuous band with an intensity maximum at 3450 Å. was to be attributed to an excited ammonia molecule decomposing on emission. No evidence is yet available to account for the continuum at 5100 Å., but if it should also be shown to be due to an ammonia molecule dissociating with emission, then reaction (1) would account for the glow.

The energy involved in the reaction associated the formation of hydrazine in ammonia discharges [1]

$$ {}^1\Delta\, NH + NH_3 = N_2H_4 \qquad . \qquad . \qquad . \qquad (2)$$
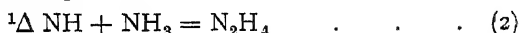
and is nearly large enough to account for the intensity maximum of the glow. This reaction is, however, excluded for the reason that it fails to account for the enhancement of the glow by molecular hydrogen.

If the molecule responsible for the $\alpha$ band, or that part of it in the neighbourhood of 5000 Å., were concerned in producing the glow, it is likely that at $-180°$ the emission would be continuous. Unfortunately, the emitter of the $\alpha$ band is not known, although it is generally assumed [7] to be $NH_2$. Such molecules could be formed from the decomposition of a highly excited hydrazine molecule. There remains the possibility that the reaction concerned is

$$2\, {}^1\Delta\, NH + {}^1\Sigma\, H_2 = N_2H_4 + 135 \text{ k. cals.} \qquad . \qquad . \qquad (3)$$

which would be favoured by low temperature in the gas phase, and might also occur on a surface at $-180°$, since this would provide a high local concentration of ${}^1\Delta$ NH molecules. The large energy involved would almost certainly cause decomposition of the hydrazine. Assuming Sidgwick's value for the energy of the N—N link [12] in hydrazine, 36 k. cals., an excited hydrazine molecule formed by reaction (3) could decompose into two $NH_2$ molecules, each excited on the average to 50 k. cals. This amount is again about 6 k. cals. lower than that corresponding to the observed intensity maximum of the glow ; for the reasons already mentioned the calculation of the energy involved in reaction (3) is un-

[8] Mulliken, *Rev. Mod. Physics*, 1932, 4, 1.

[9] Lunt, Mills and Smith, *ibid.*, where details of calculation are given.

[10] Mitchell, *J.A.C.S.*, 1927, 49, 2699.

[11] Russell and Lapraik, *J.C.S.*, 1881, 39, 168 ; Ellis, *J. Franklin Inst.*, 1929, 208, 507.

[12] Sidgwick, Sutton, and Thomas, *J.C.S.*, 1933, 432.

certain to at least this amount. Reaction (3) thus affords an explanation for the glow, its faintness, and its enhancement by molecular hydrogen, providing it is accepted that the $\alpha$ band of ammonia, or that part in the neighbourhood of 5000 Å. is due to an $NH_2$ molecule ; the low temperature and the random relative velocities of the two $NH_2$ molecules resulting from the decomposition of a hydrazine molecule would account for the continuous nature and symmetrical intensity maximum of the emission.

Additional evidence that part of the $\alpha$ band spectrum is due to the $NH_2$ molecule is afforded by the diffuse light emitted from the reaction between atomic hydrogen and hydrazine in which some of the brighter lines of the $\alpha$ band have been distinguished.[5]

It appears that the mechanism suggested by Gedye and Rideal [13]

$$H + N_2H_4 = NH_3 + NH_2 \qquad . \qquad . \qquad . \qquad (4)$$
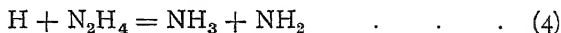
would explain the kinetics, as well as that proposed by Dixon.[5] Assuming the energy of the $NH_2$—H link to be about 85 k. cals., the energy evolved in reaction (4) is 49 k. cals., which is only 5 k. cals. short of that necessary to account for the line of shortest wave-length belonging to the $\alpha$ band which was identified by Dixon, 5200 Å. For reasons already cited, the discrepancy cannot be regarded as serious.

It is also known that at suitable low pressures and low current densities hydrazine is formed by discharges in streaming ammonia, under which conditions the $\alpha$ band is lacking or extremely faint in the spectrum of the discharge. When the current density is increased so that little or no hydrazine is detectable in the outgoing gas, the $\alpha$ band is strongly emitted.[1] It therefore appears that the $\alpha$ band arises from fragments of the hydrazine molecule produced by electron collision. Moreover, under these conditions, the decomposition does not appear to follow the reverse course of the synthesis [reaction (2) above] since when the $\alpha$ band is relatively intense the $^1\Pi - {}^1\Delta$ NH band is weak or absent.

It appears that there are only two possible reactions (1) and (3) which would account for the glow, the balance of evidence undoubtedly favouring reaction (3). If in fact reaction (3) is responsible for the glow, there is considerable additional support for the view that the $\alpha$ band, or some part of it, is due to emission by an excited $NH_2$ molecule, and the function of the low temperature surface in producing the glow is to effect a local high concentration of $^1\Delta$ NH molecules.

## Summary.

It has been confirmed that a blue glow occurs when the gases from a discharge in a stream of highly purified ammonia at low pressure are led over a surface cooled to $-180°$ C. The mechanism most consistent with the available data is that the emission arises from two excited $NH_2$ molecules resulting from the decomposition of a hydrazine molecule itself formed from the reaction between two $^1\Delta$ NH molecules and a hydrogen molecule in the ground state.

[13] Gedye and Rideal, *J.C.S.*, 1932, 1160.

# THE SCHUSTER BANDS OF AMMONIA.

By R. Winstanley Lunt, J. E. Mills, and E. C. W. Smith.

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Although the Schuster bands of ammonia have been known for many years, there has been considerable uncertainty as to whether the molecule responsible for the bands contains nitrogen and hydrogen only. The experiments now described establish this composition.

The bands named after Schuster,[1] which are only known to be excited by electrical discharges, were shown by Lecoq to be double with components [2] at 5643 and 5681 Å. ; Rimmer [3] found that no trace of fine structure was detectable when examined with a dispersion of 5·5 Å. per mm. It appears unlikely on account of the narrowness of the bands that they could be attributed to a molecule decomposing on emission.

In Schuster's original experiments a stream of moist ammonia was used, and it was noticed that the bands disappeared rapidly when the gas flow was stopped. Rimmer used an induction coil discharge, condensed and uncondensed, and ammonia dried over calcium chloride.[3] In each case water vapour must have been present. More recently Kwei examined the spectrum of ammonia in a discharge between a hot cathode and a cylindrical anode,[4] the ammonia was evaporated from aqueous solution and dried over solid KOH. He failed to detect the bands except when water vapour or oxygen was added to the ammonia, they then appeared when the potential between cathode and anode was 70 volts. It appears from the text, although no specific statement was made, that in all experiments stationary gas was used. He also found that the bands appeared when the liquid air was removed from a trap in similar experiments on nitrogen-hydrogen mixtures. From these results he concluded that water or oxygen was essential to the development of the bands. It seems likely, however, that the trap at — 180° collected all the ammonia synthesised from the nitrogen-hydrogen mixture, and that the release of this ammonia temporarily effected the development of the pressure conditions necessary to excite the bands. It will be seen later that Kwei's failure to detect the bands in ammonia was probably due to the particular type of discharge used. The significance to be attached to Kwei's claims is greatly diminished by his failure to describe his experimental conditions accurately, and to reproduce photographs of the spectra observed.

The emission of the Schuster bands in streaming ammonia was also noticed by Kneser [5] and by Bredig, Koenig and Wagner.[6] Kneser gave

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[1] Schuster, *Brit. Ass. Rep.*, 1872, 76.  [2] Lecoq, *C.R.*, 1885, **101**, 42.
[3] Rimmer, *Proc. Roy. Soc.*, 1923, **103**A, 696.
[4] Kwei, *Physic. Rev.*, 1925, **26**, 537.
[5] Kneser, *Ann. Physik*, 1926, **79**, 585.
[6] Bredig, Koenig and Wagner, *Z. physik. Chem.*, 1928, **139**A, 211.

no details relating to the purity of the ammonia used ; Bredig, Koenig and Wagner used cylinder ammonia without further purification, but showed that the gas was in a high state of purity. The latter authors called attention to curious variations in the relative intensity of the components of the Schuster bands produced by varying the conditions of excitation, and also reported that the bands could not be excited by a discharge in streaming hydrazine vapour.[7]

It will be seen from this review that there is conflicting evidence concerning the composition of the gas essential to the emission of the Schuster bands, and also that in no case have any considerable precautions been taken to ensure the purity of the ammonia used. The experiments now to be described were therefore carried out, using highly purified ammonia.

## Experimental.

**Purification of Ammonia.**—The technique adopted was based on that of McElvey and Taylor.[8]   Cylinder ammonia, supplied by Messrs. Imperial Chemical Industries, Ltd., was first dried by passage over potash and anhydrous barium oxide and then liquefied. It was then fractionated and the middle fraction was dried over freshly cut hydrocarbon-free sodium for several hours at $-80°$, the hydrogen evolved being removed when necessary. The ammonia was then distilled into another vessel in which it was maintained at $-180°$ for several hours in a high vacuum in order to remove volatile impurities. The remaining gas was subjected to three successive fractionations, in each operation the middle fraction only was retained.

**Purification of Nitrogen-Hydrogen Mixture.**—This was stored in a cylinder and had the approximate composition $N_2 : 3H_2$. It was purified by passage over potash, hot copper, dried by phosphorus pentoxide, and finally passed through a trap immersed in liquid air.

## Apparatus.

Various types of discharge tubes were used. Many experiments were carried out with a tube A made of transparent fused silica tubing 25 mm. diameter and 75 cm. long, and provided at each end with side tubes of the same diameter in which were inserted internally water-cooled aluminium electrodes. These were sealed in position by means of Wood's metal, which was then covered externally with a layer of picein wax. A plane window was fused on at one end of the discharge tube, so that the discharge could be viewed " end on " as well as transversely. Ammonia was led into the discharge tube at one end by means of a side tube, connections to the ammonia reservoir being made by a ground joint ; a subsidiary connection to this side tube enabled water vapour or hydrogen to be admitted to the discharge tube, and also led to a pressure gauge. At its other end the discharge tube was connected by a ground joint to a trap at $-180°$, and to a rotary oil pump. Pressures were measured either by a manometer containing Apiezon oil or by a McLeod gauge ; in the latter case, in order to avoid diffusion of mercury vapour into the discharge tube, the connection to the gauge was effected through a tube frequently sputtered with gold, and the tap to the gauge was kept shut except when readings of the pressure were taken. All joints and taps were lubricated with Apiezon L grease.

Some experiments were carried out with a glass discharge tube B, using hollow cylindrical electrodes of vacuum melted chromium iron mounted

[7] *Cf.* also Koenig and Wagner, *ibid.*, 1929, 144A, 213.

[8] McElvey and Taylor, *Bureau of Standards*, 1923, 465.

coaxially with the main track of the discharge which was confined by a tube 7 mm. diameter and 40 cm. long. A quartz ozoniser provided with a window so that the discharge zone could be viewed " end on " was also used. A few experiments were carried out using a straight dull-emitter filament surrounded by a coaxial cylindrical anode, and in some a grid was used in order to work with electrons of known velocities.

Alternating potentials in the frequency range, 50 to 500 cycles per second, were used for exciting discharge tubes A and B. The spectra were recorded by a Bellingham and Stanley No. 2 Spectroscope on Ilford panchromatic plates.

## Experimental Results.

The spectrum of a discharge in ammonia, purified as previously described, was examined over a fairly wide range of conditions of pressure and electrical excitation. No significant differences were observed between 50 and 500 cycle excitation.

With discharge tubes A and B at pressures above about 5 mm. Hg, the Schuster bands were always to be seen in the photographs of the discharge spectra provided the streaming velocity of ammonia was high and the current density low, thus confirming the results of earlier workers on streaming ammonia. The observation of Bredig, Koenig and Wagner that the relative intensity of the two components of the Schuster bands depends on the conditions of excitation was also confirmed ; this phenomenon will be discussed in a subsequent paper.

No appreciable difference was noticed in the appearance of the Schuster bands when cylinder ammonia was used instead of the highly purified ammonia. Before admitting the latter to the discharge tube this was subjected to a prolonged heavy discharge in a continuous stream of dry hydrogen at low pressure to remove water adsorbed on the walls, and finally evacuated to $10^{-6}$ mm. Hg. In order to exclude the possibility that the ammonia had become contaminated with water vapour from the walls of the glass tubing through which it was led to the discharge tube, it was admitted in one experiment through a 2-metre length of 1 cm. bore glass tubing from which water vapour absorbed on the walls had been removed, firstly by the passage of a discharge in hydrogen at low pressure, using external electrodes, and subsequently by baking out *in vacuo*. Furthermore, for this experiment a sample of the purified ammonia was subjected to a second drying over sodium and subsequently re-fractionated. Even under these stringent conditions the intensity of the Schuster bands remained undiminished in the spectrum of the discharge. It is known that very minute traces of water vapour in a discharge are readily revealed by the appearance of the OH bands ; a significant index of the dryness of the ammonia used in the experiments described above is afforded by the fact that in no case were these bands detected on the spectrograms. Experiments were also carried out on ammonia containing amounts of water vapour varying in partial pressure from a fraction of 1 mm. to several mms. In the corresponding spectrograms no correlation could be traced between the relative intensities of the Schuster and OH bands.

In an ozoniser discharge with the same range of ammonia pressures and flow rates as used for tubes A and B, the Schuster bands were also observed.

On the other hand, with the diode or triode discharge, no certain emission of the Schuster bands was observed. It was, however, impossible to run these discharges at pressures greater than about 1 mm. Hg. at which the attainable ammonia flow was relatively low, due to the low efficiency of the oil pump. It appears, therefore, that Kwei's failure to observe these bands in ammonia is connected with the type of discharge used.

Using the same range of pressure and streaming velocity as in the above experiments on ammonia, observations were also carried out on nitrogen-hydrogen mixtures, but in no case was any emission of the Schuster bands
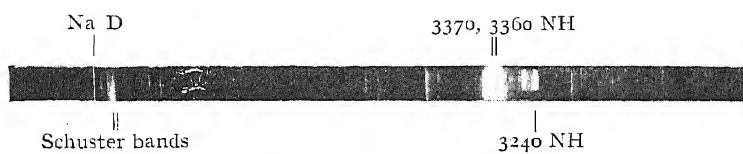
Na D               3370, 3360 NH

Schuster bands            3240 NH

Fig 1.

detectable.   In particular, it was not possible to verify Kwei's claim that these bands can be excited in such a mixture when water vapour is also present ; a possible explanation of Kwei's observation has already been suggested on page    .

A typical spectrogram of the A.C. discharge between cold electrodes in streaming ammonia is reproduced in Fig. 1 with a copper comparison spectrum.   Discharge tube B was used, the ammonia pressure when the discharge was not excited being 12·5 mm. Hg.

In agreement with earlier observations, it will be noticed that the Balmer lines are absent, and the second positive spectrum of nitrogen is weakly developed.   The $^1\Pi - {}^1\Delta$ NH band at 3240 Å. is present, in addition to the usual triplet bands at 3360, 3370 Å.   In no case in our experiments has the emission of the Schuster bands been recorded without that of the NH band.   The failure of earlier workers to notice the emission of this band is doubtless due to its proximity to the well-known triplet bands ; the earliest photographic record of this band in streaming ammonia is to be found in the experiments of Hamburger.[9]   The emission of the Na D line (as in the spectrum reproduced) is only noticed in glass discharge tubes.
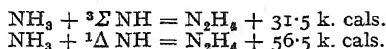
## Discussion of Results.

The ease with which the Schuster bands can be excited with great intensity in highly purified ammonia establishes that the molecule concerned in their emission contains nitrogen and hydrogen only, and the intensity of emission indicates that the transition concerned is unlikely to involve a change of multiplicity ; the fact that in our experiments these bands have never been observed without the simultaneous emission of the $^1\Pi - {}^1\Delta$ NH band suggests that there may be a connection between the appearance of the Schuster bands and the production of metastable NH molecules.

Although no data are yet available for hydrazine, its salts are diamagnetic, so that there is little reason to doubt that the ground state hydrazine is a singlet.   This ground state can be considered as derived from an ammonia molecule and the lowest singlet state ($^1\Delta$) of NH ; the corresponding value for the heat of dissociation of hydrazine[10] is about 56 k. cals.   The formation of hydrazine in discharges may then be assumed to occur at collisions between ammonia and $^1\Delta$ NH molecules.

It is not known whether the $^1\Pi$ NH molecules are produced directly

[9] L. Hamburger, *Dissertation*, Amsterdam, 1917.

[10] A fairly satisfactory value for the heat of dissociation of NH may be obtained by taking the mean of the average value of the binding energy of $NH_3$ 82·8 k. cals., and that calculated by Bates[1] on the basis of the value preferred by Mecke and Badger[2] for 102·2 k. cals. ; this leads to the value 92·5 k. cals. Mulliken estimates the difference between the $^1\Delta$ and $^3\Sigma$ NH levels to be about 25 k. cals.[3]   The corrected value for the heat of formation of hydrazine given by Berthelot and Matignon[4] is $N_2 + 2H_2 = N_2H_4 - 1\cdot3$ k. cals. : and Herzberg's recent value for the heat of dissociation of nitrogen is 169·3 k. cals.[5]   From these quantities and from the heat of formation of ammonia from its elements, 9·3 k. cals., it may easily be shown that[6] :—

$$NH_3 + {}^3\Sigma\, NH = N_2H_4 + 31\cdot5 \text{ k. cals.}$$
$$NH_3 + {}^1\Delta\, NH = N_2H_4 + 56\cdot5 \text{ k. cals.}$$

[1] Bates, *Z. physik. Chem.*, 1931, **A**, 329.
[2] Mecke and Badger, *Trans. Farad. Soc.*, 1929, **25**, 935.
[3] Mulliken, *Rev. Mod. Physics*, 1932, **4**, 7.
[4] Berthelot, *Ann. Chim. Physique*, 1893, **28**, 126.
[5] Herzberg, *Z. physik. Chem.*, 1934, **B26**, 1.
[6] *Cf.* Willey, *Trans. Farad. Soc.*, 1934, **30**, 241.

by electron impact on ammonia molecules or by excitation of $^1\Delta$ NH. Since the time between collisions in many experiments in which the $^1\Pi - {}^1\Delta$ NH band is observed is less than $10^{-7}$ sec., collisions will occur between $^1\Pi$ NH and $NH_3$ molecules. It is possible that such collisions could lead to an excited state of the hydrazine molecule.

Corresponding to the attractive ground state of $N_2H_4$ derived from $NH_3$ and $^1\Delta$ NH, there will be a repulsive state. If the curvature of the line representing the energy of this state as a function of the inter-nuclear distance were very small in the neighbourhood of the equilibrium nuclear distance of a supposed stable state derived from $NH_3$ and $^1\Pi$ NH, then transitions to the repulsive state would show a small diffuse broadening comparable to that observed in the Schuster bands. Since the $^1\Pi$ NH level is 87 k. cals. above $^1\Delta$ NH, and since the Schuster bands correspond to an energy difference of 50·6 k. cals., it would follow that the heat of dissociation of the supposed upper stable state of $N_2H_4$ is $87 - 50\cdot6 = 36$ k. cals. This value is not unreasonable in relation to that for the ground state, 56 k. cals. This suggestion for the mechanism of the emission of the Schuster bands does not, however, appear to afford an explanation of the shift of relative intensity of the two component bands produced by changes in the discharge current.

The mechanism suggested above for the synthesis of hydrazine accounts for the Schuster bands appearing only when there is a relatively small decomposition of ammonia in the discharge (high streaming velocity), for these are the conditions favouring the emission of the $^1\Pi - {}^1\Delta$ NH band, and also favouring collisions between $NH_3$ and both $^1\Pi$ and $^1\Delta$ NH molecules. From considerations of the conservation of electron spin momentum, this mechanism is more probable than one involving collisions between $NH_3$ and triplet states of NH. It would also explain the observation that the emission of the Schuster bands has been found to be a good criterion for the conditions favouring the synthesis of hydrazine in ammonia discharges.[6],[7]  The failure to excite these bands by streaming hydrazine through a positive column [6],[7] is probably due to the excitation of states involving a change of multiplicity.

The mechanism suggested also provides an explanation for the absence of the Schuster bands from discharges in streaming nitrogen-hydrogen mixtures, for under these conditions the concentration of ammonia is very low. The absence of the Schuster bands from discharges using dull emitter cathodes in ammonia is certainly attributable in part to the low pressures and streaming velocities necessitated by the apparatus available.

It is conceivable that $N_2H_2$ molecules of short life might be formed from a collision between two NH molecules and by analogy with oxygen at least two $N_2H_2$ levels might be anticipated. It appears unlikely that $N_2H_2$ molecules are concerned with the emission of the Schuster bands because when the streaming velocity in the discharge is reduced to a value such that these bands cannot be detected and the ammonia is almost completely decomposed, the relative intensities of the $^1\Pi - {}^1\Delta$ and $^3\Pi - {}^3\Sigma$ NH bands are not greatly altered. The α band of ammonia appears in ammonia discharges at lower streaming velocities than are necessary for the emission of the Schuster bands, and under such conditions little or no hydrazine is formed.[6][7]  It has been suggested that this band is emitted by $NH_2$ molecules ; [12] if this were so, then its appearance

[12] Hulthén and Nakamura, *Nature*, 1927, **119**, 235.

in ammonia discharges could be attributed to the decomposition of hydrazine initially formed in the discharge into two such molecules.

### Summary.

It has been shown that the molecule responsible for the Schuster bands contains nitrogen and hydrogen only. It has been suggested that the synthesis of hydrazine in discharges occurs at collisions between ammonia and the singlet states of NH molecules. This suggestion affords a possible mechanism for the emission of the Schuster bands, and is in accordance with the known chemical and physical data connected with the appearance of the band and the synthesis of the hydrazine.

# THE MECHANISM OF SELF-PROPAGATING CHAIN REACTIONS.

By K. K. Andreew and J. B. Chariton.

A number of chemical reactions exhibit the property of self-propagation. A reaction, started at one point, spreads throughout the whole mass of the substance. In certain cases (the detonation of explosives) the linear velocity of propagation becomes so great that it can only be explained by a chain mechanism, as already noted by Garner.[1] Thus, for example, in the case of trinitrotoluene with a detonation velocity of $6 \cdot 7 \times 10^5$ cm./sec. and a mean inter-molecular distance of $6 \cdot 2 \times 10^{-8}$ cm., the reaction front traverses this interval in $9 \times 10^{-14}$ sec.; *i.e.*, in a time comparable with the minimum life of an active molecule. It is clear that a stationary state in the reaction front is only possible if each elementary act in the reaction provokes, in a time interval of $10^{-13}$ sec., an elementary act in the next molecular layer along the direction of advance. This, however, is in fact chain propagation.

Now, the existence of infinite single chains in more or less stable explosives is impossible, since the life of such an explosive would be negligible.

In fact, as a result of the Maxwellian distribution of energy, a considerable number of molecules would undoubtedly have more than the activation energy even at normal temperatures. If, now, the resulting decomposition of the molecule led to the formation of an infinite chain, a simple calculation will show that the half-period value for the decomposition of such a substance would be of the order of a few minutes. In exactly the same way, the evidence from experiments on the action of

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[1] *Trans. Far. Soc.*, 1930, **26**, 590.

various agents (α-particles,[2] X-rays,[3] electrons,[4]) which undoubtedly decompose individual molecules, but which do not lead to decomposition of the explosive as a whole, proves that the disintegration of a single molecule is not sufficient to start an infinite chain. Thus, on the one hand, single chains cannot become infinite in explosive substances whilst, on the other, the enormous speed of detonation points to its chain-like character.

In order to remove this contradiction it is necessary to suppose that the propagation of a detonation is carried, not by single chains, but by a *group of chains* giving a chain front or *macro-chain,*[5] formed (spontaneously or artificially) as a result of a definite degree of localisation in time and space of chain centres or of elementary acts of the reaction which give rise to the centres.[6] Even under conditions where the formation of infinite single chains is impossible (*i.e.*, when the probability of the continuation of the single chain $\alpha < 1$), macro-chains may develop. In fact, the length of an individual chain as a component of a macro-chain is determined, not only by the probability of its own continuation, but also by the conditions of interaction with the other component chain ; *i.e.*, by the additional probability of branching, which depends upon the simultaneous interaction of products of the reaction of the individual single chains, these products being rich in energy.[7] As a result of this additional probability of the branching, not only may chains composing a macro-chain become infinite in length (probability of continuation $\alpha = I$), but also under certain conditions, the branching may assume such proportions that a uniform surface density of centres is preserved during the expansion of the localisation.

Let us examine the behaviour of a localisation of chain centres surrounded by the unchanged material of the explosive, and let us suppose for simplicity that the centres are closely packed in a certain spherical volume of radius $R$. After a certain time $\tau$ (of the order of $10^{-13}$ sec.) new centres will appear in the surface layer contiguous with the localisation. If the number of new centres formed from $N$ centres, in the case of simple chain reaction, is $M < N$, then the number of centres appearing

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[2] Ebler, *Ber.*, 1910, **43**, 2613 ; Garner, *J.C.S.*, 1933, 1398.

[3] Günther, Lepin and Andreew, *Z. Elektrochemie*, 1930, **36**, 218.

[4] Kallmann and Schränkler, *Naturwiss.*, 1933, **26**, 379 ; Muraour, *Chimie et Industrie*, 1933, **30**, 39.

[5] *C.R. Acad. Sci. U.R.S.S.*, 1934, **1**, 404.

[6] The assumption that detonation is brought about as a result of the simultaneous reaction of neighbouring molecules was first applied to the thermal decomposition of lead azide and mercury fulminate by Garner (*J.C.S.*, 1931, 2126 ; *Proc. Roy. Soc.*, 1933, **139**, 594). In a more general form this assumption was postulated by H. Muraour (*Chimie et Industrie*, 1933, **30**, 39), on the basis of the fact that the decomposition of a single molecule does not lead to the decomposition of the explosive as a whole.

Muraour, however, does not connect it with the chain theory of propagation of detonation—he is, moreover, even an opponent of the latter (*Chimie et Industrie*, March, 1933 ; *J. Chim. Physics*, 1934, **31**, 139). Similar ideas have been put forward several times by N. N. Semenov (*Z. physik. Chem.*, 1928, B **1**, 204) ; *J. Physic. Chem.* (*russ*), 1931, **2**, 430) and others who laid stress on the importance of the concentration of initial centres in the production of inflammation and detonation.

[7] Thus for the example, in the chain reaction between hydrogen and chlorine, a triple collision between a molecule of chlorine and two HCl particles which have only just been formed and which are carrying a considerable part of the reaction energy may lead to the splitting of the chlorine molecule into atoms, whilst the energy carried by a single HCl particle might be insufficient to do so (see N. N. Semenov, *Chemical Reviews*, 1929, **6**, 361).

in the layer under consideration will be $4\pi R^2\sigma M/N$, where $\sigma$ represents the number of molecules per cm.$^2$. The total number of molecules in the layer is $4\pi(R + d)^2\sigma$ where $d$ is the mean distance between molecules. Thus the relative density of centres in the layer, *i.e.*, the ratio of the number of centres to the total number of molecules is

$$\eta_0 = 4\pi R^2\sigma\frac{M}{N} : 4\pi(R + d)^2\sigma = \frac{M}{N} \cdot \frac{R^2}{(R + d)^2} \quad . \qquad . \quad (1)$$

or

$$\eta_0 = \alpha \cdot \frac{R^2}{(R + d)^2}, \quad \text{where} \quad \alpha = \frac{M}{N}.$$

It is clear from this formula that $\eta_0$, although it increases with $R$, will always be less than unity for any value of $R$, *i.e.*, the relative density of centres in the front will fall and the localisation will be dissipated. However, in practice, there will be an interaction between the individual chains, as a result of which $N$ centres will give rise to $M'$ centres instead of $M$, where $M' > M$ and, in this way, the ratio $M'/N = \zeta$ may become greater than unity. The relative density of centres of reaction, taking into account interaction, will then be

$$\eta = \zeta \cdot \frac{R^2}{(R + d)^2}. \qquad . \qquad . \qquad . \qquad . \quad (2)$$

Further, since the probability of branching, as a result of interaction, depends to a large degree on the distance between the centres (the distribution density of the chains) the relative number of centres

$$\frac{(M' - M)}{N} = \zeta - \alpha$$

due to branching will be higher the greater $\eta_0$, *i.e.*, the greater $R$. Thus, with the growth of the radius of the localisation, $\zeta$ increases and, starting from some value $R = R_k$ will satisfy the equation

$$\zeta \cdot \frac{R_k^2}{(R_k + d)^2} = \eta = 1, \quad . \qquad . \qquad . \qquad . \quad (3)$$

*i.e.*, the relative density created in the monomolecular layer adjacent to the localisation will be equal to the original value. This means that, when $R = R_k$ (and still more so when $R > R_k$), the closely packed front of the localisation will advance, preserving its original density. If $R < R_k$ the expansion of the localisation will be accompanied by a diminution in the density of the centres at the surface, and as a result the localisation will be dissipated.

Let us now try to estimate the effect of the surface density of the centres on their interaction, thus obtaining an estimate of the value of the critical radius of a localisation.

It is known [8] that if a single chain is developing with the formation of particles carrying energy $\epsilon$ equal to $\dfrac{Q + E}{n}$ (where $Q$ is the heat of reaction, $E$ the energy of activation, and $n$ the number of particles formed in each elementary act) then the probability of branching is determined by the concentration of molecules of unchanged substance possessing energy $U_1 = E - \epsilon$. This concentration is proportional to $e^{-U_1/RT}$. In

[8] N. Semenov, *Chemical Reviews*, 1929, **6**, 361.

the same way we can assume that if two chains are proceeding in close proximity then, in addition to the activation discussed above, it is possible that activation will also take place as a result of the collision of two particles, carrying energy $\epsilon$ from the two chains, with a molecule of the unchanged substance. In this case those molecules may be activated whose energy exceeds $E - 2\epsilon$, and the concentration is then determined by the expression $e^{-U_2/RT}$ where $U_2 = E - 2\epsilon$. Similarly, the activation probability in the case of the collision of three particles carrying energy $\epsilon$ will be proportional to $e^{-U_3/RT}$, where $U_3 = E - 3\epsilon$.

Thus the presence of neighbouring chains increases the probability of branching. Further, it follows from the formulæ that this probability varies exponentially with the energy of the interacting particles. It is easy to see that if the chains are sufficiently separated from one another so that the particles suffer several collisions before interacting, then the energy of the particles will be appreciably less,[9] and there will be a corresponding decrease in the probability of branching. Therefore, interaction will only assume importance in the development of localisation when the active centres are very closely packed, i.e., when $\eta_0$ is very close to unity, and, thus, the critical radius cannot be too small. In order to arrive at an approximate value of the lower limit for $R_k$, we can proceed as follows :

In so far as it is necessary to assume the possibility of the formation of infinitely long macro-chains in explosives, it is clear that single chains of finite length may also develop. Further, it is obvious that during the propagation of a single chain there is a certain probability that it will branch as a result of the interaction of the products of the reaction of two consecutive links. This probability will be of the same order as the probability of the interaction of two chains proceeding at a distance of two intermolecular distances, i.e., for a frontal density of chains $\eta_0 = 0.5$. Even at comparatively high temperatures (as, for example, in the case of lead azide which decomposes without detonation at 290° C.) this probability remains less than unity for the whole chain, and less than $1/\nu$ for a single link.

Since the expression for the probability of branching is of the form $e^{-U/RT}$, it follows from the above that the critical increment $U$ cannot be small, and consequently when the temperature is reduced considerably the probability of branching by interaction decreases many times and will become quite insignificant in comparison with $1/\nu$. At the same time, it is possible for detonation to occur even at the temperature of liquid air. This means that its occurrence is connected with the forma- of a localisation, in any case at low temperatures, in which $\eta_0$ is consider- ably greater than 0.5. Let us now calculate the extent which the localisa- tion must assume in order that $\eta_0$ shall exceed this figure.

If the spherical localisation is composed of $m$ centres, and if the molecules are uniformly distributed in the form of a cubic lattice so that the inter-molecular distance is $d$, then the volume of the localisation will be $md^3$, and for large values of $m$ the ratio $\dfrac{R^2}{(R + d)^2}$ can easily be shown to be

$$\left(\frac{3m}{4\pi}\right)^{2/3} \bigg/ \left[ \left(\frac{3m}{4\pi}\right)^{1/3} + 1 \right]^2 \qquad . \qquad . \qquad . \quad (4)$$

See e.g., Jeans, *Dynamical Theory of Gases*, p. 260, Cambridge, 1921.

In the case of small values of $m$ (of the order of a few units) it is necessary simply to group the $m$ centres in various ways and calculate the mean number of possible neighbours.

However, formula (4) leads to values very close to those obtained in such a way, and it can, therefore, also be applied to the case of small $m$ values. For $m = 10$ and for simplicity writing $\alpha = 1$ we get $\eta_0 = 0.33$. For $m = 50$, $\eta_0 = 0.5$. Thus the lower limit to the number of centres composing a fluctuation must not be less than 50, in any case at low temperatures. It is at present difficult to determine the actual value of $R_k$ and the corresponding value of $m_k$. We can only be certain that the greater the energy of the elementary reaction, the fewer the parts in the molecule over which this energy is distributed and the smaller the energy of activation the smaller they will be. In other words, those factors which assist the development of single chains will lead to smaller values of the critical radius. It might, therefore, be thought that, in initiating explosives, where these factors are more favourable than in the case of secondary explosives,[10] the critical dimensions of the fluctuation would be appreciably less. This deduction is well supported by the greater mechanical sensitivity and ease of detonation in initiating explosives.

If the initiation of a detonation takes place spontaneously, $i.e.$, if the corresponding localisation is formed as a result of a fluctuation, then the probability of this happening must be determined by the conditions governing the formation of the latter. Let us examine the simplest case of an explosive whose decomposition is mono-molecular. Let $n_0$ be the number of molecules per c.c., and $n = f(n_0)$ be the number of active centres. These latter may be formed in various ways, $e.g.$, as a result of the Maxwell-Boltzmann distribution corresponding to the given temperature, or as a result of external disturbance—a shock, friction, light, etc.

Let us calculate the number of coincidences occurring in one second when $m$ active centres appear in the immediate neighbourhood of one another, $i.e.$, when the distance separating each of them is of the order of the mean inter-molecular distance. In the case of $m = 2$, this will simply be the number of cases per second when an active molecule finds itself in the neighbourhood of any other active molecule, $i.e.$, within a sphere of volume $v_1$ described around the latter. The total volume of these spheres per c.c. will be $nv_1$. The number of active molecules formed every second in unit volume is $\dfrac{n}{\tau}$, whereas $\tau$ is the life of an active molecule. Of these, a fraction

$$q_2 = \frac{n}{\tau} \times nv_1 \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \quad (5)$$

will appear alongside centres which are already active, thus giving rise to a " doublet " fluctuation.

In order to calculate the number of " triplet " fluctuations, we first find the concentration of doublets, which must clearly be equal to the product of $q_2$ and the time of duration of a doublet. This life of a doublet we can take as being practically equal to $\tau$, so that the concentration becomes $v_1 . n^2$. Then, just as in the previous case, we can describe a sphere of volume $v_2$ round each of the doublets and obtain the number of triplet fluctuations $q_3$ (per cm.$^3$ per sec.) as the number of active centres formed in all the elementary volumes $v_2$.

[10] K. K. Andreew, *Sov. Physic.*, 1933, 4, 120.

Consequently,

$$q_3 = v_1 n^2 v_2 \times \frac{n}{\tau} = \frac{v_1 v_2}{\tau} n^3 \qquad . \qquad . \qquad . \qquad (6)$$

Similarly, the number $q_m$ of fluctuations containing $m$ active centres will be given by

$$q_m = \frac{v_1 v_2 \cdot \cdot \cdot v_{m-1}}{\tau} n^m. \qquad . \qquad . \qquad (7)$$

The number $n$ represents the equilibrium number of active centres created by some influence or other. In the case of a chain reaction, with which we are here concerned, $n$ will be considerably greater, since each active centre produces $v - 1$ new centres (where $v$ is the chain length), and as an approximation we may put the concentration of centres equal to $vn$, so that formula (7) becomes

$$q'_m = \frac{v_1 v_2 \cdot \cdot \cdot v_{m-1}}{\tau} (vn)^m \qquad . \qquad . \qquad (8)$$

From (7) it is seen that the probability of formation of a fluctuation consisting of $m$ active centres is proportional to the $m$th power of their concentration.[11] Clearly the magnitude of this concentration is a function of the parameters, characterising the intensity of the impulse, which creates the active centres. Unfortunately, the form of this function is not known for the majority of ways of exciting an explosion (friction, a shock, etc.). It is only known in the case of " thermal " activation as a result of the Maxwell-Boltzmann distribution of energy. Here the number of active molecules is $n_t = n_0 e^{-E/RT}$, and (7) becomes

$$q_m = \frac{v_1 v_2 \cdot \cdot \cdot v_{m-1}}{\tau} (n_0 e^{-E/RT})^m, \qquad . \qquad . \qquad (9)$$

whilst for a chain reaction we get

$$q'_m = \frac{v_1 v_2 \cdot \cdot \cdot v_{m-1}}{\tau} (vn_0 e^{-E/RT})^m \qquad . \qquad . \qquad (10)$$

From this hypothesis as to the possibility of forming a localisation as a result of a fluctuation, it might appear that there is a real possibility of spontaneous starting of an explosion at any temperature, for example, during the storage of explosives.

Let us, however, examine the actual probability of such an occurrence. Experiment shows that, even at comparatively high temperatures, approaching the flash-point, explosives tested under appropriate conditions decompose, in the vast majority of cases, without explosion,[12] i.e., during the time of decomposition the probability of the formation of the critical fluctuation is small in comparison with the probability of non-detonating decomposition. Let us see how this probability changes with the lowering of temperature.

From formula (9) we may conclude that the probability $dV$ of the appearance of a fluctuation in a certain mass of explosive in a time $dt$ is determined by the expression

$$dV = pM e^{-mE/RT} dt,$$

[11] For large values of $m$ the actual values of probabilities will be smaller than those given by (7) because the neighbouring molecules cannot acquire excessive energy independently of one another.

[12] See W. E. Garner, *J.C.S.*, 1931, 2123, and other investigators.

where $p$ is a constant and $M$ the mass of the sample. In the case of a decomposition following a first order reaction law

$$M = M_0 e^{-kt},$$

where $k$ is the velocity constant.

In this case the probability of the formation of a fluctuation during the whole time occupied by the decomposition will be

$$V = \int dV = \int_0^\infty p M_0 e^{-mE/RT} e^{-kt}\, dt = p M_0 e^{-mE/RT}/k$$

as

$$k \approx e^{-E/RT},$$

$$V \approx e^{-(m-1)E/RT}.$$

Consequently the probability of the appearance of a sufficient number of centres to form a critical fluctuation (and we have seen that this number is by no means insignificant) will be extremely small at the usual temperatures of storage, even when taken over the whole time occupied by the isothermal decomposition of the explosive, so that the possibility of spontaneous detonation under these conditions is not real.

However, even a purely " thermal " detonation has not an elementary fluctuational origin. In fact, from (9) which determines the probability of formation of a fluctuation, it follows [13] that, in so far as this probability is the same in any volume element in a homogeneous explosive, the average time-lag before explosion should be inversely proportional to the total mass of the substance. Further calculation shows that the mean square deviation of the observed time-lags from the mean should be twice the square of the mean, or $\delta^2 = 2\tau^2$. Finally, the logarithm of the time-lag should be inversely proportional to the absolute temperature. This latter relationship, which has actually been found, prompted H. Muraour [14] to advance the hypothesis that thermal explosions are due to the simultaneous reaction of several molecules at one point. However, it was shown by the authors [13] that the first two conditions necessary for such a mechanism were not fulfilled. A possible cause of this is to be found in the fact that equation (9) assumes that the system remains unchanged throughout the time of observation, so that the probability of explosion in a given time interval is constant. Actually, however, it can be shown by simple experiment that, during the time preceding explosion, complex changes of a chemical and physical character take place in the explosive which profoundly affect the probability of explosion. As a result, the time-lag is determined chiefly by the laws regulating the course of these changes, and does not obey the two first of the above-mentioned relations derived from formula (9).

If, however, thermal explosion does not show the regularities demanded by the fluctuation hypothesis, on account of the influence of the time on the explosion probability, it is possible to imagine other cases where this influence is negligible. Thus, for example, if we consider the case of the stationary burning of an explosive, where there is a certain probability of the process going over to detonation, as happens in a number of substances, then it is clear that this probability, in so far as it is connected with a continuously re-establishing stationary front, does not change with the time. Under these conditions the times of burning before the detonation, or the corresponding lengths burned, up to the

[13] Andreew and Chariton, *Chimie et Industrie*, 1934, **31**, 1040.
[14] *Chimie et Inudstrie*, 1933, **30**, 39.

instant of detonation, should follow the law deduced from the fluctuation mechanism. The experimental data [15] so far obtained are insufficient to decide the question as to whether these regularities exist.

In the same way, we may assume that the regularities characteristic of the fluctuation mechanism will appear in cases where states with a high fluctuation probability are created very rapidly as, for example, when excitation takes place as a result of a mechanical blow, or of sudden intense illumination in light-sensitive systems. Here, it is interesting to note that the results of experiments with excitation by mechanical shock show a considerable scatter, and the variation of the percentage of explosions with the energy of the shock is expressed by the Gaussian law, according to the latest data.[16] On the other hand, thermal explosions of the same substances give a much smaller scatter in the values of the time-lag and minimum temperature of explosion, in spite of the fact that much less care was devoted to reproducing identical experimental conditions than was given in the case of excitation by mechanical shock.

However, certain observations of Taylor and Weale (the fact that the ratio between the energy of the blow required for a given percentage of explosions and the area over which the energy is supplied is independent of the total area) show that the process of mechanical explosion, if it has a fluctuational character, is in any case more complex than that envisaged in the elementary fluctuation mechanism. Finally, the excitation of explosions by bombardment with energy-rich particles—ions,[17] products of an explosion,[18] etc., afford a very interesting opportunity of testing the fluctuation hypothesis. It is a simple matter to calculate the probability of a fluctuation of $m$ centres due to the simultaneous impact of a definite number of bombarding particles and to compare this with the actual probability of detonation. It is possible, here, by changing the energy and concentration of the particles and the parameters of the bombarded substance to study the phenomena in greater detail.

## Summary.

The enormous velocity of detonation indicates that propagation takes place by means of chains. At the same time the existence of infinite single chains in explosives is inadmissible.

The concept of macro-chains developing as a result of a formation of a localisation of chain centres is introduced, and it is shown that, starting from a certain minimum critical size, it is capable of infinite stable growth. An attempt has been made on the basis of the conditions required for the interaction of chains to estimate the critical size of a localisation. The probability of the formation of a localisation as a result of a fluctuation is then considered, as well as various cases where it might serve as a cause of explosion, in particular thermal explosion where, however, the regularities demanded by the elementary fluctuational mechanism are not fulfilled.

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[15] Laffitte and Patry, *C.R.*, 1931, **193**, 1339; Andreew, *C.R. Acad. Sci. U.R.S.S.*, February, 1935.
[16] Taylor and Weale, *Proc. Roy. Soc.*, 1932, **138**, 92.
[17] Kallmann and Schränkler, *Naturwiss.*, 1933, **26**, 379.
[18] Beljaev and Chariton, *C.R. Acad. Sci. U.R.S.S.*, 1934, **3**, 167.

# THE LOWER LIMIT OF IGNITION OF HYDROGEN-OXYGEN MIXTURES.

## By W. E. GARNER AND H. J. WILLAVOYS.

*Received 6th March,* 1935.

Since the commencement of this research in 1930, there have been published several papers on the lower limits of ignition of hydrogen-oxygen mixtures.[1] The researches described in the above papers cover nearly the same ground as our investigation, but there are nevertheless certain points of interest arising out of the research which makes publication desirable.

Hydrogen-oxygen mixtures in the molar ratios 3 : 1, 2 : 1, 1 : 1, and 1 : 2 have been studied over the range of temperatures 350-600° C. and the curves for the lower limits have been traced down to the critical ignition pressures. In a few cases, it has been found possible to measure upper limits also. The results, while being in general agreement with those of previous investigators, show that the lower limit is extraordinarily sensitive to the state of the surface of the containing vessel

## Experimental.

The procedure adopted for the determination of the lower limits was similar to that used by Garner and Cosslett.[2] The mixtures of hydrogen and oxygen were dried over phosphorus pentoxide, and admitted as rapidly as possible to an evacuated silica vessel which was heated to the required temperature. The hydrogen was prepared by the electrolysis of 40 per cent. caustic soda and the oxygen by heating A. R. Permanganate. Pressures were measured on a water jacketed McLeod gauge which was kept at a temperature of 45° C. to prevent condensation of water vapour. The inlet and exit tubes to the silica vessel were maintained at a temperature slightly above 45° C.

The silica vessel was 3·1 cm. internal diameter and 21 cm. long. Its capacity was 159 c.c. and its internal area approximately 210 cm.[2] Two such tubes were used in the course of the research. The inlet tube was 0·9 cm. diameter and 16·4 cm. long while the exit tube leading to the gauge was 0·3 cm. in diameter and 15 cm. long. The volume of the McLeod gauge was approximately 25 c.c. The furnace was lined with rustless steel, and gave a constant temperature over the middle region within 1-2° C.

The apparatus was calibrated by dry air which was measured in a burette, compressed into a small bulb immediately adjoining the inlet tube, and then admitted through a wide bore tube into the reaction vessel. When the explosive mixtures were admitted, if no ignition occurred, the pressures read on the McLeod gauge ten seconds after admission were the same as with air, since the amount of heterogeneous reaction that occurs is very small over a period of twenty minutes. In order to determine the lower limit of ignition, the pressures read on the McLeod after admission of the explosive mixture were plotted against the pressures obtained after admission of the same volume of air. A graph showing a series of results

[1] Hinshelwood and Moelwyn-Hughes, *Proc. Roy. Soc.,* 1932, **138A,** 311 ; Alyea and Frost, *J.A.C.S.,* 1933, **55,** 3227.
[2] *Trans. Far. Soc.,* 1931, **27,** 176.

obtained with $2H_2 + O_2$ in Tube II. is shown in Fig. 1. The dotted lines show the pressures corresponding to no ignition and complete ignition respectively. It will be noted that at the temperatures 450-550° C. the curves cross the complete ignition curve, indicating that water vapour was being adsorbed on the glass walls in spite of the temperature of these being maintained at 45° and over. The lower limits can be determined with reasonable accuracy from such curves. The upper limits could be determined in a few cases in Tube II., owing to an appreciable lag in the onset of ignition.

In the neighbourhood of the minimum explosion pressure, it was difficult to obtain reproducible results, and it was found necessary either to evacuate for a long time or to heat to a high temperature before each experiment as in the experiments on $CO + O_2$. Unless this was done, an



I.   384 – 402°.
II.  412°.
III. 425°.
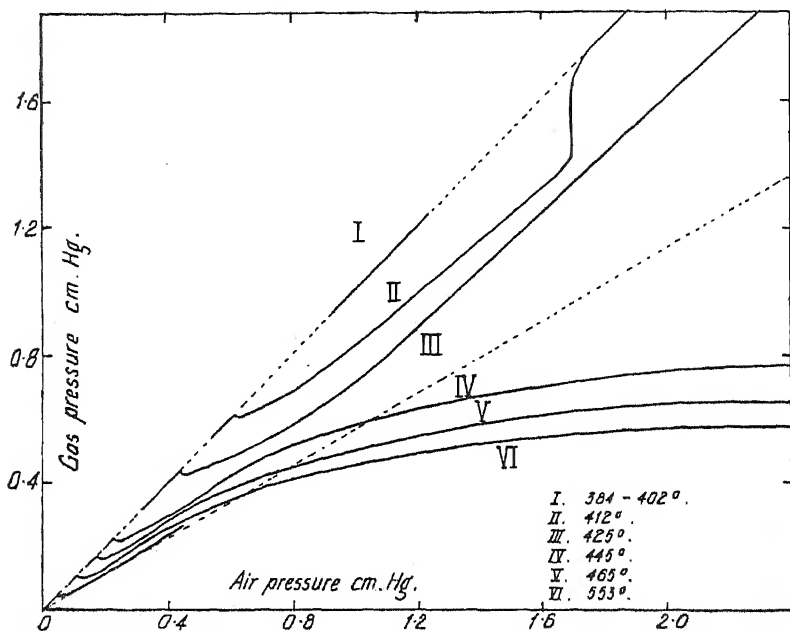IV.  445°.
V.   465°.
VI.  553°.

Fig. 1.

explosion in the tube was found to lead to a modification of the walls, such that no explosion could be obtained even at higher pressures. The reproducibility of individual results is not very good as will be seen from Fig. 3.

The extent of the combustion, as shown by the departure from the no ignition line, is very slight just above the lower limit and is never complete at any pressure at the lower temperatures. The amount of gas unburnt varies with the pressure as will be seen from the figures given below for $2H_2 + O_2$ at 425° in Tube II.

Press. Initial (cm.).

2·59  2·54  2·46  2·10  1·89  1·64  1·44  1·07  0·79  0·62  0·61  0·55  0·50  0·46

Press. Unburnt (cm.).

2·55  1·21  1·22  0·90  0·77  0·66  0·26  0·21  0·13  0·17  0·26  0·35  0·34  0·38

As the initial pressure increases, the residual pressure at first falls and then increases. The figures show clearly the operation of the two factors, deactivation by the walls, and deactivation in the gas phase, which are mainly

responsible for the occurrence of the upper and lower limits.    The above
values are probably only approximate since adsorption of water vapour
may have occurred in the gauge and the tubes leading to it.    It is possible,
however, that the pressures of water in the above experiments may be
below the critical limit for the formation of the multimolecular layer.[3]
The percentage combustion increases as the molar concentration of the
oxygen increases.

## Experimental Results.

The values for the limits are given for a range of temperatures in
Table I., for the mixtures $2H_2 + O_2$, $H_2 + O_2$, $H_2 + 2O_2$, and $3H_2 + O_2$.

### TABLE I.

| Tube. | Temp. °C. | Limit, cm. | Tube. | Temp. °C. | Limit, cm. | Tube. | Temp. °C. | Limit, cm. |
|---|---|---|---|---|---|---|---|---|
| **$2H_2 + O_2$.** | | | | | | | | |
| I | 366 | 1·26 | I | 422 | 0·260 | I | 478 | 0·154 |
| II | 384-402 | — | II | 425 | 0·435 (2·60) | I | 505 | 0·120 |
| I | 404 | 0·39 | I | 444 | 0·220 | I | 512 | 0·132 |
| II | 412 | 0·62 (1·73) | II | 445 | 0·220 | II | 553 | 0·100 |
| II | 413 | 1·80 (1·99) | II | 464 | 0·165 | I | 608 | 0·040? |
| **$H_2 + O_2$.** | | | | | | | | |
| I | 365 | 0·89 | II | 421 | 0·27 (2·50) | I | 488 | 0·130 |
| I | 374 | 0·67 | ·II | 423 | 0·27 | II | 493 | 0·110 |
| I | 397 | 0·46 | I | 456 | 0·180 | II | 565 | 0·080 |
| II | 400 | — | II | 463 | 0·150 | I | 590 | 0·060? |
| II | 414 | 0·41 (1·66) | | | | | | |
| **$H_2 + 2O_2$.** | | | | | | | | |
| II | 350-382 | — | II | 392 | 0·235 (1·462) | I | 441 | 0·135 |
| I | 372 | 0·31 | II | 404 | 0·164 | II | 451 | 0·108 |
| II | 386 | 0·292 (1·335) | II | 418 | 0·142 | II | 493 | 0·104 |
| II | 388 | 0·418 (1·400) | II | 440 | 0·150 | II | 497 | 0·068 |
| **$3H_2 + O_2$.** | | | | | | | | |
| I | 309-368 | — | I | 455 | 0·280 | | | |
| I | 394 | 0·540 | I | 571 | 0·032 | | | |

The two silica vessels gave identical values for the lower limits at high tem-
peratures and low pressures, but there was a marked difference in their
behaviour at low temperatures and high pressures.    Tube I. gave lower
values than Tube II. for the limits in the region 400-425° C., and values for
the upper limit could only be obtained with Tube II.    The results with
both tubes are included in the tables, those for the upper limit being
bracketed.

The results for three mixtures in Tube II. are plotted in Fig. 2.    These
curves are remarkable for the blunt nose of the flame peninsula.

**Lower Explosion Limits.**—The lower limits over the range 3 : 1
to 1 : 2 decrease as the proportion of oxygen increases, as will be seen from
the summary given below.    The limits for the 3 : 1 mixture are less re-
liable than the others since fewer measurements were made with this
mixture.

[3] *Cf.* McHaffie and Lenher, *J.C.S.*, 1925, **127**, 1559 ;  Lenher, *J.C.S.*, 1926,
1785.

TABLE II.

| Temp. °C. | | 425. | 450. | 475. | 500. | 550. | 600. |
|---|---|---|---|---|---|---|---|
| Lower limit. cm. | 3 : 1 | 0·40 | 0·30 | 0·23 | 0·17 | 0·07 | — |
| (Diameter of | 2 : 1 | 0·38 | 0·21 | 0·15 | 0·13 | 0·09 | 0·05 |
| tube 3·1 cm.) | 1 : 1 | 0·27 | 0·18 | 0·14 | 0·115 | 0·08 | 0·05 |
| | 1 : 2 | 0·14 | 0·12 | 0·10 | 0·08 | 0·04 | — |

Hinshelwood and Moelwyn-Hughes [1] find that in a silica tube 1·8 cm. in diameter, the values for the last three mixtures are 3·45, 3·3, and 3·2 mm. respectively at 550° C. These values are considerably higher than ours, even taking into account the fact that the diameters of the tubes were 1·8 and 3·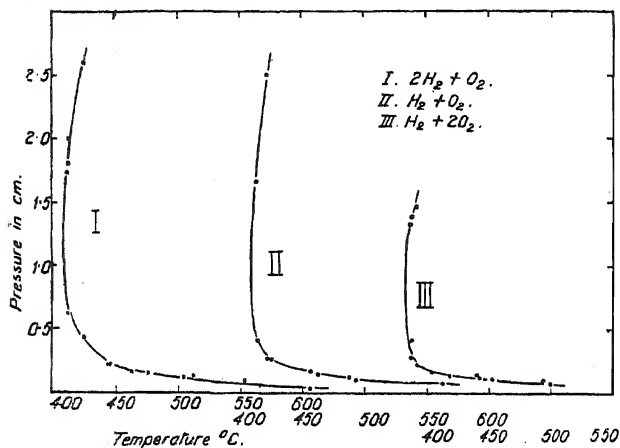1 cm. respectively.* Alyea and Frost,[1] using a pyrex tube, washed with a 10 per cent. solution of potassium chloride, obtained still higher values. It is clear, therefore, that the lower limits are very dependent on the nature of the surface of the walls of the containing vessel.



I. $2H_2 + O_2$.
II. $H_2 + O_2$.
III. $H_2 + 2O_2$.

FIG. 2.

The Upper Limit.—Only a few values were obtained, and these indicated that the upper limit increases with increase in the oxygen content of the gas. This is in agreement with the observations of other workers.[4]

The Critical Explosion Pressure.—It was not possible to determine this pressure very exactly since in Tube II. the flame peninsula had a very blunt nose. It lies between 0·6 and 1·8 cm. for $2H_2 + O_2$, between 0·4 and 1·7 cm. for $1H_2 + O_2$, between 0·4 and 1·4 cm. for $H_2 + 2O_2$. Thus for a 3·1 cm. tube changes in composition have but a small effect on the critical explosion pressure. The minimum temperature of ignition is, however, lowered from 410-390° on passing from a 2 : 1 to a 1 : 2 mixture.

The Stationary Reaction.—The order of the heterogeneous reaction always lay between the first and zero and in spite of this the rate of reaction was found to be proportional to the initial pressure. In these respects the surface reaction behaves analogously to that of carbon monoxide and oxygen on silica.

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* For a 3·2 cm. silica tube at 550°, Hinshelwood and Moelwyn-Hughes obtain 2·85 mm. for the lower limit of $2H_2 + O_2$.

[4] Cf. Semenoff, *Chemical Kinetics and Chain Reactions*, 1935, p. 207.

## Discussion.

The values obtained for the lower limit in silica vessels by different observers show very little numerical agreement.    Those observed in the present investigation are lower than any previously obtained for silica tubes, and they differ from those of Hinshelwood and Moelwyn-Hughes [1] in that they show an appreciable fall with increase in temperature.

**Temperature Coefficients of the Lower Limits.**—The plots of the limiting pressures against $1/T$ are given in Fig. 3 together with some values obtained by Semenoff.    The curves for Tube II. at the lower temperatures are shown by dotted lines, and it will be seen that the curvature for Tube II. is greater than for Tube I.    The activation energy falls from a value greater than 15,000 down to 7,000 calories at the highest temperatures.    Both Semenoff and Hinshelwood, for a narrower range of temperatures than those shown in Fig. 3, have obtained a value of 14,000 for the activation energy, but Semenoff gives reasons for believing that this value is too high.[*]

According to the investigations of Hinshelwood and his co-workers, variations in the pressure limits can be ascribed (a) to differences between the capacities of various walls for breaking the reaction chains, and (b) to variations in the
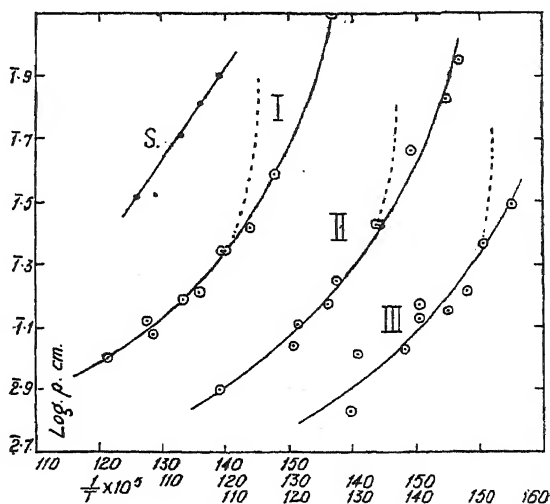


FIG. 3.—S. Semenoff.    I. $2H_2 + O_2$.    II. $H_2 + O_2$
III. $H_2 + 2O_2$.

rate of production of water by the heterogeneous reaction, the water acting as a negative catalyst and raising the lower explosion limit. The latter is of special importance in silver tubes, where the flame peninsula very largely disappears.[5]    The low values obtained by us in silica tubes could be interpreted as due to a high reflectivity of reaction centres by the walls and the curvature of the graphs in Fig. 3 as due to a decrease in the reflective power of the walls with fall in temperature.    The two tubes employed in the research gave identical values for the limits at high temperatures, where the surface would be freer from adsorbed gas, and only showed deviations in the region of the minimum ignition temperature where difficulties due to variation of the surface are found to occur very frequently.

The experimental observations made above can without any difficulty be accounted for on the current theories of the ignition of mixtures

[*] *Loc. cit.*[4], p. 250.
[5] Hinshelwood and Moelwyn-Hughes, *Proc. Roy. Soc.*, 1933, **139A**, 521.

of hydrogen and oxygen. It is, however, admitted that these theories are imperfect in that they fail to account for the downward movements of the flame peninsula which occur when a large number of reaction centres are introduced into the gas.* It is probable that effects produced artificially by the addition of active centres from the outside will also be present in experiments on the initiation of flame by thermal means. Surfaces vary in the ease with which they catalyse gaseous reactions, and hence it is to be expected that the density of the reaction chains started from the surface will vary from case to case. If the density of the chains be small, then the values obtained for the upper and lower limits should approach the ideal as predicted by the chain theory. In extreme circumstances, however, the density may be so high as to produce thermal effects, especially at high pressures, and if these thermal effects are produced near the walls of the reaction vessel, then the influence of inert gases may not be in accord with the theory. Such effects may have occurred in the investigations on carbon monoxide,[2] or carbonyl sulphide [6] and on carbon monoxide and nitrous oxide.[7] Thermal effects are unlikely in the region of the lower limits of hydrogen and oxygen mixtures for the pressures are so small. There still remains, however, the possibility of an interaction between reaction chains. Thus there is a possible alternative explanation of the variations met with in the lower limits. The low values obtained in the present investigation may be due to a high measure of interaction between the reaction chains, and the curvatures of Fig. 3 may be caused by a decrease in the interaction with fall in temperature.

**The Variation of the Lower Limit with Changes in Composition.**—There seems to be much uncertainty with regard to the way in which the limiting pressures vary with changes in composition of the gas. According to Hinshelwood and Moelwyn-Hughes [1] $p_{H_2} \times p_{O_2}$ is a constant at the limit but according to Frost and Alyea [1] between 40 and 70 per cent. of oxygen, the limit is unaffected by the hydrogen and depends only on the partial pressure of the oxygen. Table III. shows that in the present investigation, at constant temperature, $p_{O_2}$ is practically constant between 25 and 66·6 per cent. $O_2$. The greatest deviations occur near the critical pressure of ignition. The lower limit obviously depends more on the oxygen pressure than on any other single factor.

TABLE III.—Oxygen Pressures at the Lower Limit.

| Temp. °C. | | 425. | 450. | 475. | 500. | 550. |
|---|---|---|---|---|---|---|
| per cent $O_2$ : | 25 | 0·10 | 0·075 | 0·058 | 0·043 | — |
| | 33·3 | 0·125 | 0·070 | 0·050 | 0·043 | 0·03 |
| | 50 | 0·135 | 0·090 | 0·070 | 0·058 | 0·04 |
| | 66·6 | 0·093 | 0·080 | 0·067 | 0·053 | 0·03 |

The expression $p_{O_2}(p_{H_2} + p_{O_2})d_2 = k$, which is advocated by Semenoff, does not fit the above results at all satisfactorily.

* Semenoff, *loc. cit.*[4], p. 261.
[6] Bawn, *J.C.S.*, 1933, 145.    [7] Bawn, *Trans. Far. Soc.*, 1935, **31**, 461.

## Summary.

The lower limits for the ignition of hydrogen-oxygen mixtures in the molar ratios 3 : 1, 2 : 1, 1 : 1, and 1 : 2 have been determined in silica vessels for the temperatures 350-600° C. In a few cases, the upper limits have also been measured.

The values for the lower limits are much lower than those obtained by previous workers and the equation, log $p_1 = ke^{E/RT}$, is found not to be in agreement with the results obtained. The activation energy varies from 7,000 at the high temperatures to approximately 15,000 calories at the low temperatures. The values of the limits near the critical ignition pressure are very much affected by the state of the silica surface.

In agreement with Frost and Alyea it has been found that the lower limit is more dependent on the oxygen pressure than on any other single factor.

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# ABSORPTION OF LIGHT BY GASEOUS CHLORINE IN THE WAVELENGTH REGION 5040 Å.U. TO 5320 Å.U.

BY F. W. JONES, B.Sc., AND W. SPOONER, B.Sc.

It has been known for some time that gaseous chlorine shows a continuous absorption spectrum at wavelengths less than approximately 4787 Å.U. and a band absorption spectrum at wavelengths greater than that limit [1] but no attempt appears yet to have been made to decide to what extent the continuum invades the region of the band absorption. This is of interest in connection with the photochemical reaction of chlorine and hydrogen. For when a molecule of chlorine absorbs light in the continuum, the molecule is dissociated. On the other hand, discontinuous (band) absorption alters the state of the molecule without dissociating it.

The chlorine band absorption spectrum is very complicated, with much overlapping of lines, but places in the spectrum can be found apparently free from line absorption. These places have been examined for continuous absorption by a spectrophotometric method.

A glass tube, 136·7 cm. long and 2·5 cm. diameter, having a side tube attached which could be immersed in liquid air, was filled with chlorine at atmospheric temperature and pressure. By means of a suitable optical system the light from a motor headlight lamp was rendered parallel, and the parallel beam, after passing through the chlorine tube was focussed upon the slit of a Rowland diffraction grating. This was adjusted so that

[1] H. Kuhn, *Z. Physik,* **39,** 77, 1926.

light of wavelength 5200 Å.U. fell upon the centre of the photographic plate.

Two photographs and density marks were taken on each plate.   The first photograph was taken with the chlorine in the tube ; the second with the chlorine condensed in the side tube by liquid air.   In both cases exposure time and lamp current were exactly the same.   All photographs were taken at room temperature, in this case 18° ± 2° C.   In the interests of accuracy, it was found more convenient to take the density marks for the calibration of the photographic plate with the aid of a small diffraction grating.

The plates were micro-photometered, using a Moll type recording micro-photometer, firstly through the chlorine absorption spectrum, and then through the continuous spectrum of the lamp.   At the wavelengths apparently free from line absorption, density marks obtained from step-slits of various widths [2] were also micro-photometered, and intensity, density curves plotted.   From these curves (log $I$ — log $I_0$) was found. The intensity of the light transmitted by the chlorine,

$$I = I_0\, \epsilon^{-\alpha c d},$$

where    $I_0 =$ incident light intensity.
$c =$ concentration of chlorine in gram-mols. per litre.
$d =$ thickness of column in cms.
$\alpha =$ molar absorption coefficient.

Thus $\alpha$, the coefficient of continuous absorption, can be calculated.   The values obtained are tabulated below.

MOLAR ABSORPTION COEFFICIENTS.

| Wavelength Å.U. | Plate 1. | Plate 2. | Plate 3 (a) | Plate 3 (b). | Plate 4. | Average. |
|---|---|---|---|---|---|---|
| 5040 | — | 0·073 | 0·073 | — | — | 0·073 |
| 5065 | — | ·084 | ·075 | — | — | ·080 |
| 5100 | 0·083 | ·078 | ·070 | — | — | ·077 |
| 5120 | ·065 | ·049 | ·042 | — | — | ·052 |
| 5150 | ·044 | ·036 | ·026 | 0·032 | 0·019 | ·031 |
| 5190 | ·028 | ·025 | ·019 | ·013 | ·018 | ·021 |
| 5225 | ·022 | — | — | ·013 | ·017 | ·017 |
| 5270 | ·017 | — | — | ·004 | ·013 | ·011 |
| 5300 | — | — | — | ·003 | ·005 | ·004 |
| 5320 | — | — | — | ·003 | — | ·003 |

Halban and Siedentopf [3] have measured the absorption coefficients of chlorine at a number of wavelengths ;  the dispersion employed was, however, relatively small, and would not enable band and continuous absorption to be measured separately.   One would consequently expect that the values for the absorption coefficients which they obtain would be higher than those obtained in the investigation now being described. In the region which we have investigated, only one value of $\alpha$ is given by Halban and Siedentopf, namely $\alpha = 0·0452$ at a wavelength of 5090 Å.U. and this is actually lower than the value obtained by inter-polation of our results at the same wavelength $(\alpha = 0·078)$.   That considerable errors must be present in such measurements as these is evident from the fact that an error of 1 per cent. in the measurement of the intensity of the light transmitted by the chlorine $(I)$ would cause

[2] L. S. Ornstein, J. W. H. Moll and H. C. Burger, *Objective Spectralphoto-metrie*.
[3] Halban and Siedentopf, *Z. physik. Chem.*, **103**, 80, 1922.

an error of 4 per cent. in our value of $\alpha$ and $6\frac{1}{2}$ per cent. in that of Halban and Siedentopf, at the above wavelength.   At a wavelength of 5300 Å.U. the error in $\alpha$ produced by 1 per cent. error in $I$ in the two cases would be $23\frac{1}{2}$ per cent. and 38 per cent. respectively.   It should, however, be pointed out that Halban and Siedentopf used a special differential method intended to minimise these errors.

Interpolation of Halban and Siedentopf's results at other wavelengths shows that their values for the (total) absorption coefficients are of the same order as those given by our measurements made at the same wavelength, the wavelengths being those at which the spectrum is apparently free from band absorption lines.

In spite of the low accuracy of our measurements it may reasonably be concluded that those chlorine band lines which are resolved in the first order spectrum of a 10 ft. grating contribute but little to the total absorption in the wavelength region 5040 Å.U. to 5320 Å.U.   The results show that between the band lines in this region is absorption extending at least as far as 5320 Å.U.; this absorption appears to be continuous, though the possibility that it consists of a large number of close lines is not excluded.

## Summary.

The absorption coefficient of chlorine has been measured at a number of wavelengths where there appears to be no band line absorption, between $\lambda = 5040$ Å.U. and 5320 Å.U.   It is found that a measurable absorption occurs at these points.   This absorption appears continuous when the spectrum is examined in the first order of a 10-foot grating ; it is, however, possible that greater resolution would show that it is due to a number of close lines.

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# THE LATENT HEAT OF FUSION OF EQUILIBRIUM MIXTURES OF LIGHT AND HEAVY WATER.

By L. Jacobs

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*Communicated by* E. K. Rideal.

A direct determination of the latent heat of fusion of heavy water and of various mixtures of light and heavy water has been carried out using a Nernst calorimeter.

## The Calorimeter.

The calorimeter, designed for 0·5 gm. of heavy water, consisted of a thin silver cylinder 1 cm. diameter and about $1\frac{1}{2}$ cms. high with a German

silver neck which could be sealed by soldering round its screw top.    The
water was introduced into the dried weighed calorimeter with the aid
of an " Agla " syringe and the increase in weight measured.    The screw
top of the calorimeter was soldered in position.    To check that no evapora-
tion had occurred during the soldering the top was unsoldered at the end
of the experiments and the calorimeter was then weighed before and after
removal of the water.    Unless the initial and final masses of water agreed
to within 1 or 2 parts in 1000 the whole series of experiments was rejected.
(See columns 4 and 5, Table I.)

A coil of platinum wire ($\frac{1}{5}$ mm. diameter) wound round the outside of
the calorimeter, the windings being insulated from it and from each other
by silk, was used both as heating element and resistance thermometer.
To reduce heat losses from the calorimeter it was covered on the outside
with silver foil and suspended inside an evacuated brass jacket.    The
tungsten leads to the calorimeter were sealed through a pyrex tube which
was ground on to the brass jacket.    The whole surroundings were main-
tained at a suitable constant temperature in a bath.

To reduce the cooling correction while the ice was melting, the tempera-
ture of the bath was as near as possible to the melting-point.    An ice
bath was used for ordinary ice.    For the heavy water mixtures (pure
$D_2O$ melts at 3·80° C.) a water bath was used.    The water, initially cooled
to the required temperature, was contained in a large cylindrical Dewar
vessel surrounded by ice.    The top of the Dewar vessel was covered with
trays of ice and the brass tube carrying the calorimeter jacket was cooled
by passing ice cold water through a spiral tube wound round it. . Even
so the temperature of the water rose slowly during an experiment and
the procedure finally adopted was to adjust the initial temperature of the
bath slightly below the melting-point and to follow its change with a
mercury thermometer (calibrated by the N.P.L.).

This mercury thermometer was also used to measure the temperature
coefficient of the resistance thermometer, when first ice and then water
at 16-18° C. were placed in the Dewar vessel.    The mean of several results
showed that a change of 4·64 cms. on the Bridge wire corresponded to a
1° C. change in the calorimeter temperature.    This factor was used in the
calculation of the specific heats of ice and water, but appeared only in a
small correction factor in the latent heat, which depended essentially
on the measurement of current, resistance and time.

## Electrical Measurements.

The resistance of the platinum thermometer was about 3 ohms and
was measured to $10^{-4}$ ohms by a Wheatstone Bridge arrangement.    The
two ratio arms were each about 100 ohms, and were adjusted to very
nearly equal values, their ratio being determined by interchanging them
as $\lambda = 1\cdot00047$.    The platinum coil formed the third arm and a calibrated
resistance box constructed for the purpose the fourth arm, the fine adjust-
ment being on a metre wire of manganin connecting the third and fourth
arms.    The resistance box consisted of four " 1 " ohm coils and 10 " 1/10 "
ohms coils.*    The leads to the thermometer in the third arm were com-

* The box was calibrated as follows : The zero of the wire was obtained,
by shorting the resistances at each end, 49·77 cms.    Each of the " 1 " ohm coils
and the 10 " 1/10 " coils were compared with one particular 1 ohm coil, by the
usual substitution method with a subsidiary resistance box in place of the
platinum thermometer.    The " 1/10 " ohm coils were inter-compared and each
obtained as equivalent to a length of bridge wire.    Finally the particular 1 ohm
coil, in terms of which all the resistances of the box were known, was compared
with the standard 1 ohm coil of a Tinsley Ratio Box, which had been recently
measured by the maker and guaranteed accurate to 1 in 1000.    The calibration
showed that 43·42 cms. change on the bridge wire corresponded to a change of
resistance of 1/10th ohms (true) in the box.    This method of calibration, using
the standard 1 ohm in the same position that the thermometer ultimately occupied

pensated by placing equal dummy leads in the fourth arm. Thermo-electric effects were eliminated by reversing the current.

To obtain the effective resistance for calculating the heat supplied the measured resistance $R$ of the platinum coil was corrected for the exposed ends of the coil which were attached to the external leads. It was assumed that half the heat developed in the exposed ends went to heating the calorimeter, the other half being lost to the leads and so the effective resistance $R$ to be used was

$$R = R^1\{1 - x/(2 \times 85\cdot 2)\} \quad . \quad . \quad . \quad . \quad (1)$$

where $x$ = total exposed length of coil in cms. and $85\cdot 2$ cms. = total length of coil, $x$ was about 1 cm.

The " heating " current for the calorimeter coil (about $0\cdot 1$ amp.) was obtained from accumulators and remained constant to within 1 in a 1000 during an experiment (2-3 hours). The total bridge current was measured by a potentiometer and the current through the coil could be calculated from it since all the resistances were known. To obtain the natural heating due to radiation, etc., a much smaller "measuring" current $(8 \times 10^{-3}$ amps.) was used.

## The Course of an Experiment.

The calorimeter and container were placed in a freezing mixture at about $- 20^\circ$ C. When the calorimeter had reached the temperature of the freezing mixture the air was pumped out of the container, the last traces being subsequently removed by a charcoal tube immersed in liquid air.

The freezing mixture was then replaced by the " constant temperature " bath. The calorimeter and ice commenced to warm up (curve AB, Fig. 1) and this natural heating was followed to determine the heat loss constant. The heating current was then turned on and the heating of the ice to the melting-point (curve CD), the melting of the ice (DE) and the rise of temperature of the water (curve EF) followed



FIG. 1.—A typical experiment.

by the resistance thermometer. With the measuring current only the natural cooling curve for the calorimeter and water, GH, was obtained.

To make the heat loss corrections it was necessary to find the resistance of the coil when it was at the bath temperature. The curve GH was therefore followed until equilibrium was established.

Extrapolation of the natural heating curve and the electrical heating curve to the time when the current was turned on showed that with the heating current on the temperature of the coil was above that of the calorimeter (usually about $\frac{1}{4}^\circ$ C.). A similar difference was observed when the current was turned off. This is discussed later.

The melting for all the mixtures was sharp so that it was possible to estimate the melting-point at D to about $1/10^\circ$ C. These measurements agree well with those of La Mer and Baker [1] (Table I.). The comparison depends, of course, on the use of the mercury thermometer.

eliminated, to the first order, the use of the factor $\lambda$ in the future resistance measurements with the box. There was a small residual error of the order $(1 - \lambda)$ multiplied by the largest resistance interpolated on the bridge wire. The most this could amount to was about $1 \times 10^{-4}$ ohms, which was within the experimental error.
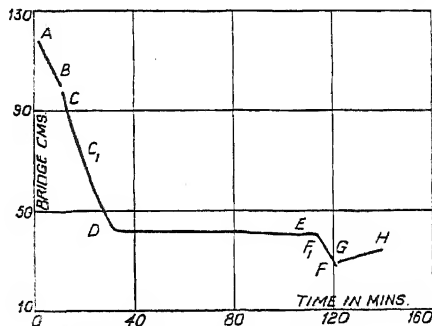
## Calculation of the Latent Heat.

The latent heat $l$, per gram is given by the equation

$$ml = \frac{i^2 R}{J}t - H_0(\theta_m - \theta_1) - H_1(\theta_2 - \theta_m) - \phi \qquad . \qquad (2$$

where $m$ = mass of water in grams

$t$ = time from a point on the curve CD (say $C_1$ at time $t_1$ temperature $\theta_1$) to a point on the curve EF (say $F_1$ at time $t_2$, temperature $\theta_2$)

$i$ = current through the heating coil

$R$ = corrected resistance of the coil (equation (1))

$J$ = mechanical equivalent of heat (4·185 joules per 15° cal.)

$H_0$ = heat capacity of calorimeter plus ice at sufficiently low temperatures for pre-melting to be negligible

$H_1$ = heat capacity of the calorimeter plus water

$\theta_m$ = melting-point of the ice

$\phi$ = cooling correction.

$\theta$ is the actual temperature of the calorimeter and $\theta'$ the bath temperature minus calorimeter temperature.   $R$, $t$, $i$ and $\theta$ were directly observed and $H_0$, $H_1$ and $\phi$ calculated from the curve as follows.

## (1) The Heat Capacity of Calorimeter plus Ice $H_0$.

This was calculated from the slope of the curve CD.   We have

$$H\frac{d\theta'}{dt} = \frac{i^2 R}{J} + k\theta' \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

where $H$ = heat capacity calorimeter plus ice at the temperature $\theta$, $k$ = natural cooling constant and the other symbols have the meaning given above.   A similar equation holds for the slope of AB,

$$H_0\frac{d\theta_0'}{dt} = \frac{i_0^2 R_0}{J} + k\theta_0' \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

The suffix O refers to the curve AB ($i_0$ = " measuring " current).

With $\frac{d\theta'}{dt}$ taken at a point very near C, $H$ was very nearly equal to $H_0$ for it varies little below 5° C. lower than the melting-point (Fig. 2).   In this case putting $H = H_0$ in (3) and eliminating $k$ from the equation so obtained and (4) we have

$$H_0 = \frac{i^2 R - i_0^2 R_0 \dfrac{\theta}{\theta_0}}{J\left(\dfrac{d\theta}{dt} - \dfrac{\theta}{\theta_0}\dfrac{d\theta_0}{dt}\right)} \qquad . \qquad . \qquad . \qquad (5)$$

from which $H_0$ was calculated.

Equation (4) then gave $k$ and hence $H$ could be deduced at any temperature from (3).   As, however, the first term on the right of (4) was about 1 per cent. of the second term it was neglected in calculating $k$, which was taken as $H_0\left(\dfrac{1}{\theta_0}\dfrac{d\theta_0}{dt}\right)$.   A similar treatment gave the heat capacity of the empty calorimeter.   The actual values obtained in two independent experiments were 0·843 and 0·866, mean = 0·855 cals. per degree.

$H$ was nearly constant at low temperatures but increased rapidly with the temperature as the melting-point was approached.   This is shown by Fig. 2 in which the specific heat of ice is plotted as a function of the temperature and has been previously observed for light ice by Nernst [2] and by Dickinson and Osbourne [3] and explained as due to pre-melting.

The heat capacity $H_0$ of the calorimeter plus ice at the lowest temperature where no appreciable pre-melting occurred was required for equation (2). The value of $H_0$ (about 1·0 cals./° C. were reproducible to about 3 to 5 per cent. for the same sample of water, the variation probably being due to the error in fixing the slope of the curve CD. As the initial temperature $\theta_1$ had to be about 4° C. below the melting to include all the pre-melting of
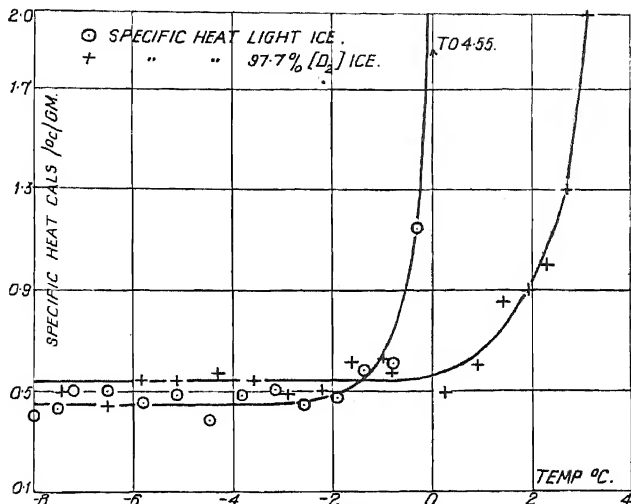


FIG. 2.—The premelting of ice.

the ice in the melting period, the value of the correcting term $H_0(\theta_m - \theta_1)$ was about 4 cals., with a possible error of about ± 0·08 calories ( ± 0·16 in the latent heat). The resulting variation in the value of the specific heat of ice was 10 to 20 per cent.—see Table I.

## (2) The Heat Capacity of Calorimeter Plus Water, $H_1$.

$H_1$ did not vary appreciably with the temperature and was deduced from the mean slope of curve EF by equation (5). $H_1$ (about 1·4 cals./deg./grm.) was reproducible to 1 per cent. and with $\theta_2 - \theta_m$ of the order of 1° C., the possible error in $H(\theta_2 - \theta_m)$ was about ± 0·01 cals. (about ± 0·02 cals. in the latent heat).

## (3) The Cooling Correction.

The two values of $k$, the cooling constant for the beginning and the end of an experiment respectively (the value of curve GH was deduced in exactly the same way as that for AB), agreed usually to within about 10 per cent. The mean of the two values of $k$ was taken and the heat lost during the period $t$ by cooling was

$$\phi = kt(\bar{\theta}_2 - \bar{\theta}_1)$$

where $\bar{\theta}_2$ = mean temperature of the calorimeter deduced from the area under the curve in Fig. 1, $\bar{\theta}_1$ = mean bath temperature also deduced by graphical integration. $\bar{\theta}_2 - \bar{\theta}_1$ was usually about 0·1 to 0·2° C. and $\phi$ was about 0·5 cals., so that the possible error in $\phi$ due to uncertainty in $k$ was about 0·03 cals. A more important source of error in $\phi$ was due to the error in determining the difference of temperature between the calorimeter and wire, for this appears directly in the estimation of $\bar{\theta}_2$. In the worst experiment from this point of view the measured differences at switching on and switching off differed by 0·11° C. giving a maximum possible error in $\phi$ of ± 0·2 cals. The error, using the mean of the two differences is certainly less than this and can safely be assumed to be not

greater than ± 0·1 cals. in this particular experiment.  In most of the experiments the difference was much less than 0·11° C.

The total possible error expected to arise from the last three terms on the right of equation (2) was thus about ± 0·1 cals. (excluding the last discussed rather uncertain correction in $\phi$), and since $m$ in that equation was about $\frac{1}{2}$ gram, a total possible error of about ± 0·2 cals. was to be expected in the latent heat per gram.  Actually, most of the experiments on the same specimen of water with different heating currents agreed to within about 0·1 to 0·2 cals. (Table I.) and carrying the heating current (time of melting) is a test of the accuracy with which the heat loss correction is made.

## Results.

The latent heat of fusion was measured for light water and equilibrium mixtures of light and heavy water containing molar fractions of 0·2967, 0·5051, 0·7636 and 0·9770 of $D_2$.  The results are summarised in Table I.

### TABLE I.

| Sp. Grav. Water. | Molar Percentage of $D_2$. | Time to Melt Ice (mins.). | Latent Heat Deduced from (a) Initial Weight | (b) Final Weight cals./gm. | Sp. Ht. Ice cals./°C./gm. | Sp. Ht. Water cals./°C./gm. | M. pt. °C. | La Mer and Baker. M. pt. °C. |
|---|---|---|---|---|---|---|---|---|
| ·9980 (21° C.) | — | 94 | 79·32 | 79·45 | ·43 | 1·02 | | |
| ,, | — | 80 | 79·38 | 79·51 | ·41 | 1·04 | | |
| 1·0304 (18° C.) | 29·67 ± ·05 | 94 | 79·09 | 79·16 | ·41 | 1·06 | 1·45 | |
| ,, | ,, | 104 | 79·29 | 79·33 | ·47 | 1·07 | 1·35 | |
| ,, | ,, | 90 | 79·10 | 79·14 | ·41 | 1·08 | 1·40 | 1·20 |
| 1·0529 (16·6° C.) | 50·51 ± ·05 | 90 | 78·54 | 78·66 | ·54 | 1·08 | 2·05 | |
| ,, | ,, | 78 | 78·46 | 78·58 | ·51 | 1·06 | 2·15 | 2·00 |
| 1·0800 (21° C.) | 76·36 ± ·05 | 90 | 77·20 | 77·34 | ·54 | 1·05 | 3·05 | |
| ,, | ,, | 96 | 77·42 | 77·57 | ·54 | 1·06 | 3·00 | 3·00 |
| 1·1036 (18·5° C.) | 97·70 ± ·05 | 80 | 76·12 | 76·17 | ·50 | 1·06 | 3·75 | |
| ,, | ,, | 90 | 76·11 | 76·16 | ·53 | 1·06 | 3·80 | |
| ,, | ,, | 106 | 76·44 | 76·49 | ·49 | 1·07 | 3·70 | 3·75 |
| | 100·00 | | | | | | | |

Extrapolated gives latent heat 76·15 cals./gram.

The mean value for the latent heat of fusion per gram of light water is 79·42, 15° cals. with a probable error of ± 0·04 cals. and a satisfactory test of the performance of the apparatus is the agreement with the result obtained by Dickinson and Osbourne.[3]  These workers give the value 79·64 15° cals., but they took the value of the mechanical equivalent of heat as 4·187 joules per 15° cal., whereas the value now accepted * is 4·185, so that their final result is 79·68 cals./gms. and this is to be accepted as a standard value since they used a large quantity of water and took all the precautions necessary to obtain an accurate result.  The difference between the present value and that given by Dickinson and Osbourne should probably be regarded as due to some systematic error in the present small calorimeter, in which case all the latent heats given should be multiplied by 1·0033.

Figure 3 shows the relation between the latent heat per gram and per

* Birge, *Review of Modern Physics*, Vol. 1, p. 1, 1929.

mol. and the molar fraction of $D_2$, the points being the mean of the values in Table I. The curves are those calculated from the theory given below.

Extrapolation of curve I. in Fig. 3 gives the latent heat of fusion per gram of $D_2O$ as 76·15 15° cals., so that the molar heat of fusion is 1525 cals. (with a probable error of ± 2 cals.).

In a recent paper La Mer and Baker [1] have calculated the molar latent heat of fusion of pure heavy water ($D_2O$) by two indirect methods. The application of Seltz equations (4) for perfect solid solutions to their data for the freezing-point of mixtures of light and heavy water yields a value of 1600 cals./mol. By comparing the depression of the freezing-point of $H_2O$ and $D_2O$ (98·6 per cent.) by potassium chloride, and assuming the osmotic pressure coefficient was the same in both solutions, a second value was obtained of 1510 cals./mol. They pointed out that the discrepancy between the two values is very likely due to the neglect of the equilibrium $H_2O + D_2O \leftrightarrows 2HDO$ in the Seltz theory and the second value is more likely to be accurate. In their second series of experiments the heavy water was exposed to the atmosphere so that the percentage changed from 99·5 at the beginning to 98·6 at the end. Taking the molar latent heat 1510 cals. as referring to the percentage 98·6, their result lies 14 cals. below the present curve (Fig. 3).

Since the present work was completed, Bartholomé and Clusius [10] have measured the latent heat of fusion of 99·7 per cent. heavy water using a Bunsen Ice Calorimeter and their value is 1522 ± 8 cals. per mol. This is in agreement with the present value of 1524 ± 2 for 99·7 per cent. heavy water.

Bernal [5] has recently calculated a theoretical value 1·5 kilo calories for the molar heat of $D_2O$ from his model of the water molecule.[6]

The primary object of this investigation was to de-



FIG. 3.—The latent heat of fusion.

termine the latent heat, the specific heats of ice and water only appearing in the small correcting terms previously discussed. It was thus sufficient, for these terms, to know the heat capacities of calorimeter plus ice and calorimeter plus water to within a few per cent. As has already been pointed out, this results in large fluctuations in the values of the specific heats shown in Table I. (because of the large heat capacity of the calorimeter) and it would be unwise to attempt to draw conclusions as to any possible trend of the specific heats.

## Discussion of Results.

If the mixture of light and heavy water be considered as an ideal solution containing $H_2O$, HDO, $D_2O$, theoretical equations for the curves of Fig. 3 can be deduced.

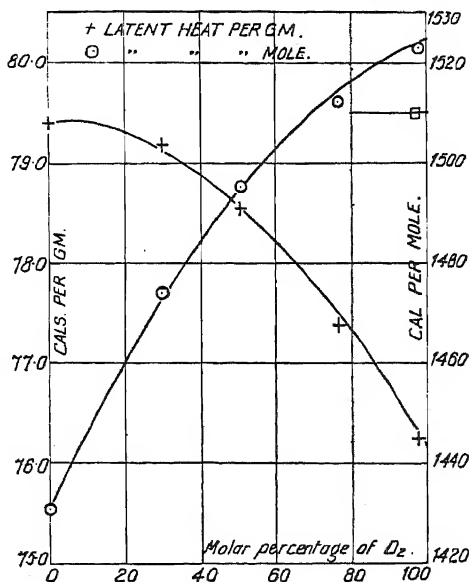The molar latent heat of fusion of an ideal mixture containing mol.

fractions $N_1$, $N_2$ and $N_3$ of three substances (in this case $H_2O$, $D_2O$, HDO respectively) with molar latent heats $L_1{}^t$, $L_2{}^t$, $L_3{}^t$ respectively is

$$L^t = N_1 L_1{}^t + N_2 L_2{}^t + N_3 L_3{}^t \quad . \quad . \quad . \quad (6)$$

where 
$$N_1 + N_2 + N_3 = 1 \quad . \quad . \quad . \quad (7)$$

The superscript $t$ denotes the value at the temperature $t°$ C.

For any pure substance

$$L_0{}^t = L_0 + C_0(t - t_m) . \quad . \quad . \quad . \quad (8)$$

Where

$L_0{}^t = $ molar latent heat at $t°$ C.
$L_0 = $ molar latent heat at the melting-point $t_m$.
$C_0 = $ (molecular heat of liquid $-$ molecular heat of solid) assumed independent of the temperature.

Thus if $L_1$, $L_2$, $L_3$ are the molar latent heats of fusion of $H_2O$, $D_2O$ and HDO at their melting-points $t_1$, $t_2$, $t_3$ respectively, and if we assume that $C_0$ has the same value $C$ for the three substances (cf. Table I.) * equation (6) becomes using (8) and (7)

$$L^t = \sum_{\lambda=1}^{r=3} N_r(L_r - Ct_r) + Ct \quad . \quad . \quad . \quad (9)$$

The $N$'s are further related by the equation

$$\frac{N_3{}^2}{N_1 N_2} = k, \quad . \quad . \quad . \quad . \quad (10)$$

where $k$ is the equilibrium constant.

With any given mixture having a known molar percentage of $D_2$, $N_1 N_2 N_3$ can be calculated from equations (7) and (10), and substitution of these values in (9) enables $(L_3 - Ct_3)$ to be deduced from the measured molar heat of fusion. The results of the calculation are given in Table II. $k$ has been taken as $3 \cdot 12$ at $0°$ C. (Farkas [7]) and $C$ as $9 \cdot 06$ cals. per mol., the value deduced from the standard specific heats of ordinary ice and water.

The errors in the last column are probable errors due to the probable errors in $L_t$ and to $\pm 0 \cdot 05$ in the molar percentage

TABLE II.

| Molar Per Cent. $D_2$. | $L^t$ cals./mol. | $L_3 - 9 \cdot 06\, t_3$. |
|---|---|---|
| — | $1430 \cdot 8 \pm 0 \cdot 7$ | |
| $29 \cdot 67$ | $1473 \cdot 9 \pm 0 \cdot 6$ | $1497 \pm 4$ |
| $50 \cdot 51$ | $1495 \cdot 5 \pm 0 \cdot 6$ | $1496 \pm 3$ |
| $76 \cdot 36$ | $1512 \cdot 8 \pm 1 \cdot 2$ | $1487 \pm 6$ |
| $97 \cdot 70$ | $1523 \cdot 5 \pm 1 \cdot 2$ | $1468 \pm 24$ |
| $100 \cdot 00$ | $1525 \quad \pm 2 \cdot 0$ | |

of $D_2$. The values of $L_3 - 9 \cdot 06 t_3$ are constant to within the experimental error, the mean of the first three is 1493 cals. The last value is, of course, subject to considerable uncertainty on account of the small amount of HDO in the mixture. The theoretical calculated using the mean value 1494 are shown in Fig. 3. $t_3$, the melting-point of DHO

* The specific heat differences for the mixtures given in Table I. are all approximately the same within about 10 to 20 per cent. If these are the same the molecular heat differences will not be the same but will be in the ratio of the molecular weights. If the calculation is carried out on this basis the values obtained for $L_3$ do not differ by more than 1 in 1500 from those given in Table II. which is calculated on the basis of constant molecular heat differences.

cannot be measured directly. The only basis on which it can be calculated at present, as Gilfillan [8] has pointed out, is to assume $L_1$, $L_2$ and $L_3$ to be equal. The present experiments show that this assumption cannot be made. All that can be said at present is that $t_3$ probably lies between $t_1$ and $t_2$ so that $L_3$ lies between 1493 and 1527 cals. per mol.

## Summary.

The latent heats of fusion of 0, 29·67, 50·51, 76·36 and 97·70 per cent. (molar percentage of $D_2$) heavy water have been measured using about ½ gram of the water in a Nernst calorimeter. The value of 1430 of the molar latent heat of fusion $H_2O$ agrees well with the standard value 1435·5 of Dickinson [2] and Osbourne [3] (corrected for the change in the accepted value of J since they reduced their results). If the difference is regarded as due to some inherent error in the present small calorimeter all the results given should be multiplied by 1·0033. The molar latent heats are given in Table II. and shown as a curve in Fig. 4 and the molar heat of $D_2O$ was obtained by extrapolation as 1525 ± 2 cals.

A simple mixture theory gives the value of $L_3 - 9·06 t_3$ as 1494 where $L_3$ is the molar latent heat of HDO and $t_3$ is the melting-point of HDO (see Table II.).

I wish to thank Professor E. K. Rideal for suggesting this work, and for his continued interest during its course. I wish also to express my gratitude to Dr. J. K. Roberts for assistance in designing the apparatus, and advice during the research, and to Trinity College, Cambridge, for a Research Scholarship. The heavy water was prepared by Dr. A. Farkas of this laboratory.

### REFERENCES.

[1] La Mer and W. N. Baker, *J. Amer. Chem. Soc.*, 1934, **56**, 2641.
[2] Nernst, *K. Ak. Wiss. Sitz.*, 1910, 262.
[3] Dickinson and Osbourne, *Bull. Bur. Standards*, 1915, **12**, 49.
[4] H. Seltz, *J. Amer. Chem. Soc.*, 1934, **56**, 2201.
[5] J. D. Bernal, *Nature*, 1935, **135**, 231.
[6] R. H. Fowler and J. D. Bernal, *J. Chem. Physics*, 1933, **1**, 515.
[7] A. Farkas, *Heavy Hydrogen*, 181, Cambridge University Press.
[8] Gilfillan, *J. Amer. Chem. Soc.*, 1934, **56**, 2201.
[9] La Mer, Eichelburger and Urey, *J. Amer. Chem. Soc.*, 1934, **56**, 248.
[10] Bartholomé and Clusius, *Z. physik. Chem.*, 1935, **28**, 167.

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# EXCHANGE REACTIONS BETWEEN HEAVY HYDROGEN AND HYDROGEN ADSORBED IN SOLIDS.

By Adalbert Farkas and Ladislas Farkas.

The purpose of the present paper is to point out that at higher temperatures heavy hydrogen can undergo an exchange reaction with hydrogen solved or absorbed in the wall of a quartz vessel or in metals, and that this exchange can be observed even with apparently thoroughly outgassed material, when no gas is given off which could account for the appearance of light hydrogen.

From the experiments to be described below it will be seen that this exchange might affect the accuracy of quantitative experiments with heavy hydrogen and in certain cases might even preclude the investigation.

A quartz vessel of 68 cm.³ volume (volume of walls 12 cm.³) was baked out at 720° C. until less than 0·002 cm.³ (N.T.P.) was given up per hour, then filled with deuterium at 20 mm. Hg pressure. From time to time the D-content of the gas in the vessel was analysed according to the micro thermo conductivity method by withdrawing small samples of 0·003 cm.³ (N.T.P.) from the vessel.[1] Table I. shows the decrease of the D-content of the gas inside the vessel.

TABLE I.

| Time in Minutes. | D-content in Per Cent. |
|---|---|
| 0 | 100 |
| 85 | 94·6 |
| 145 | 93·6 |
| 200 | 92·3 |
| 320 | 90·1 |
| 360 | 86·5 |
| 1380 | 77·3 |

TABLE II.

| Time in Minutes. | D-content in Per Cent. |
|---|---|
| 0 | 0 |
| 60 | 3·1 |
| 140 | 5·2 |
| 220 | 7·4 |
| 1110 | 17·6 |

It can easily be seen that the amount of hydrogen appearing by interchange with deuterium in the vessel is at least five times larger than that given up in the absence of deuterium.

The quartz vessel containing deuterium was thoroughly evacuated for a considerable time and ordinary hydrogen introduced. Table II. shows that in this case the hydrogen becomes gradually " heavier."

A comparison of Table II. with Table I. shows that the exchange of hydrogen atoms proceeds approximately with the same speed if the walls be saturated with light or heavy hydrogen.

On lowering the temperature this exchange reaction becomes slower, and proceeds, e.g., at 620° C. four times more slowly.

This exchange reaction was found to complicate an investigation on the thermal reconversion of orthodeuterium [2] and the homogeneous interaction of deuterium with water vapour or of hydrogen with heavy water vapour for the following reasons.

The exchange reaction of deuterium with the hydrogen solved in the wall over the temperature range 600-700° C. proceeds much more slowly than the homogeneous conversion of orthohydrogen in the gas phase, and thus the catalytic conversion occurring through the walls is negligible. On the other hand, the rate of conversion was measured by the micro method based on the different heat conductivities of ortho and para deuterium, and therefore the appearance even of the slightest amounts of light hydrogen in the gas affected the accuracy of the measurements since the thermal conductivity is altered to a greater extent by the replacement of D-atoms in the gas by H-atoms than by the conversion of orthodeuterium into normal deuterium. This disturbing effect of the exchange reaction occurring inside the walls of the vessel could be practically eliminated by saturating the walls of the vessels with pure deuterium.

The interaction of light and heavy hydrogen has an activation energy somewhat greater than 60 kg. cals. and the reaction proceeds only with a measurable speed at about 800° C.; here the exchange reaction has a

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[1] Cf. also R. H. Crist and G. A. Dalin, *J. Chem. Physics.*
[2] A. Farkas and L. Farkas, *Proc. Roy. Soc.*, 1934, A **144**, 467.
[3] A. Farkas, L. Farkas and P. Harteck, *Proc. Roy. Soc.*, 1934, A **144**, 481.
[4] A. Farkas and L. Farkas, *Proc. Roy. Soc.*, A (*in the press*).

considerable velocity also. In this case it was not possible to separate the homogeneous and heterogeneous reactions.

Table III. shows the progress of the exchange reaction in a mixture of 16·5 mm. $H_2O$ + 23·5 hydrogen containing 77·0 per cent. deuterium at 810° C.

In the next experiment 77 per cent. deuterium was introduced into the vessel without the addition of water and in this case also a decrease in the D-content of the gas was observed, which proceeded with half the speed of the reaction in the presence of water and was obviously due to an exchange with hydrogen in the walls of the vessel. For this reason the investigation of the interaction of the deuterium and water could not be carried out.

TABLE III.

| Time in Minutes. | Per Cent. D. |
|---|---|
| 0 | 77·0 |
| 5 | 71·5 |
| 12 | 67·0 |
| 22 | 63·0 |
| 32 | 58·5 |
| 50 | 56·0 |
| 70 | 51·5 |

It is well known, especially from the results of the investigations on the thermionic and photo-electric properties of metals by Dubridge [5] and of Cassel and Glückauf, that metallic wires exposed to gases and then subjected to high temperatures *in vacuo* continue to liberate solved gases for prolonged periods of time, although a flashing process may temporarily clean the surface of the filament. Even when no gas is apparently given up at relatively high temperatures (800° C.-1000° C.) the gas content may be not inconsiderable. It has been found that exchange reactions between deuterium and hydrogen solved in metallic wires (*e.g.*, nickel, platinum and tungsten) proceed relatively rapidly, and thus provide a method for the detection and estimation of such hydrogen or deuterium.

For example, a platinum wire of 0·1 mm. diameter and 10 cm. length was baked out in high *vacuo* at 1000° C. for one hour when no measurable gas evolution could be noted. When brought into contact for one minute with 0·003 cm.³ (N.T.P.) deuterium at 600° C. the D-content of the deuterium decreased by 8·8 per cent. Then the wire was heated for a few minutes to 1000° C. in heavy hydrogen and again baked out *in vacuo*. In the next experiment 0·003 cm.³ of hydrogen was introduced into the vessel in which the wire was stretched and the wire heated to 600° C. for one minute. In this case 3·4 per cent. deuterium appeared in the hydrogen.

It should be pointed out once more that in these cases both with the quartz vessel and platinum wire the exchange reaction with deuterium was observed when *in vacuo* practically no gas was given off. Apparently the hydrogen in the quartz and in the metal is present in a strongly bound state which cannot readily be evaporated off, but which will undergo a chemical reaction when in contact with hydrogen.

Similar exchange reactions may occur when heavy water is decomposed by apparently perfectly outgassed tungsten or iron, and a slight dilution of the heavy hydrogen obtained in this manner due to the exchange must be envisaged when making quantitative experiments.

In the case of the metal wires it is found that the ortho-parahydrogen or deuterium conversion or the interaction of $H_2$ and $D_2$ according to $H_2 + D_2 = 2HD$ can be catalysed at temperatures so low that practically no exchange with hydrogen solved or absorbed in the wire can be detected. This point is being investigated in more detail.

[5] *Physic. Rev.* 29, 1927 ; 1928, 32.

## Summary.

It is shown that even thoroughly outgassed materials such as quartz vessels, platinum wires and the like contain a certain amount of hydrogen the presence of which can be demonstrated by exchange with heavy hydrogen. It is emphasised that this exchange reaction might affect the accuracy of kinetic experiments with heavy hydrogen.

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# THE HYDROLYSIS OF ETHYL IODIDE.

## By J. Greenspan, S. Liotta, V. K. La Mer.

(*Contribution from the Department of Chemistry, Columbia University.*)

In a recent paper, Moelwyn-Hughes [1] reported kinetic and stoichiometric measurements on the reaction between ethyl iodide and sodium thiosulphate. In contradiction to the work of Slator,[2] who found that one mole of alkyl halide reacted quantitatively with one mole of thiosulphate, Moelwyn-Hughes reports a molar ratio of 1 : 0·6. This finding was attributed to a side reaction between ethyl iodide and water and believed to be general for alkyl halides leading to "a complex soluble organic compound (*e.g.*, iodo-ether) in which iodine resists the usual titration reactions," so that only 70 per cent. of the iodide is determined by the Volhard method.

Since the thiosulphate replacement reactions have been studied in detail in this laboratory [3] with results which have always been in substantial agreement with Slator's pioneer work, we have carefully repeated the experiments reported by Moelwyn-Hughes.

To establish the purity of our ethyl iodide, which was distilled at atmospheric pressure, samples were saponified at 100-105° for one day in sealed tubes with 0·0258 $M$ sodium hydroxide. The resultant solutions were analysed by acid-base titration (A) to determine the HI formed, and then by the Volhard method (V) to determine iodide ion, with the following results expressed in percentage recovery :

> Experiment 1 :   100·4 per cent. (A) ;   100·0 per cent. (V),
> Experiment 2 :   99·6 per cent. (A) ;   100·4 per cent. (V),

using 0·02 $M$ ethyl iodide concentrations.

The hydrolytic reaction was carried out at 100-105° for four-and-a-half days in sealed tubes containing 0·02 $M$ and 0·04 $M$ ethyl iodide in water :

[1] *J. Chem. Soc.*, 1576, 1933.          [2] *Ibid.*, **85**, 1286, 1904.
[3] La Mer, *J. Am. Chem. Soc.*, **51**, 3341, 1929 ; La Mer and Kamner, *J. Am. Chem. Soc.*, **53**, 2832, 1931 ; La Mer and Fessenden, *J. Am. Chem. Soc.*, **54**, 2351, 1932.

Experiments on 0·02 $M$ EtI :

  (1) 99·45 per cent. (A) ;  99·78 per cent. (V),
  (2) 98·72 per cent. (A) ;  98·37 per cent. (V),
  (3)        99·9  per cent. (V).

Experiments on 0·04 $M$ EtI :

  (4) 99·8 per cent (V).
  (5) 99·9 per cent. (V),
  (6) 99·2 per cent. (V),
  (7) 97·2 per cent. (V).

Experiments 6 and 7 represent parallel experiments, the first carried out under nitrogen, the latter in the presence of air.  Tube 7 developed a dark yellow colour, doubtless due to oxidation, resulting in only 97·2 per cent. recovery as iodide, whereas the nitrogen filled tube remained colourless and yielded 99·2 per cent. recovery.

From these results we conclude that ethyl iodide is qualitatively hydrolysed at 100-105° to yield one mole of inorganic iodide per mole of ethyl iodide used, and that the results reported by Moelwyn-Hughes are incorrect.

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# REVIEWS OF BOOKS.

**Reports on Progress in Physics.** London: The Physical Society.  1934. Pp. iv + 371, with numerous illustrations.  Price 12s. 6d. net.

To review this volume adequately is an impossibility; a preliminary consideration of its pages confronts one with such a selection of subjects as Eddington's gravitational theory, fugacity, Callendar's steam tables, visual acuity, X-ray tubes and "permalloy." There can be no doubt about its comprehensiveness and the care with which it has been compiled : actually it consists of a number of special articles dealing with important aspects of Physics, such as Quantum and Wave Mechanics, Spectroscopy, Optics, Heat, Low Temperature Work, Atomic Structure and so on, together with copious references.  The excellent custom of marginal symbols is carried over from the Physical Society's tradition.  Clearly, the book is much more than a "super" version of "Science Abstracts."

It would not be quite fair, however, to suppress two criticisms, both very general and by no means applicable to every section of these Reports.

The first is that much comparatively early history seems to occupy an excessive amount of space ; it is the remnant of an epoch when one was allowed, almost encouraged, to talk of electronic orbits, empirical spectral equations and the like, now consigned to honourable storage in the attic. This tendency makes for a certain lack of reality to the physicist of 1935, trained in an atmosphere of rigid economy of mechanical concepts.  At the same time, the treatment is not nearly detailed enough to be regarded as historical.

The second comment is more difficult to make.  It is far from the reviewer's aim to be ungracious, nevertheless it is this, that in spite of all the knowledge conveyed in these pages there seems to lack some common background of profound scholarship, sheer weight of learning, call it what you will.  And it is this beyond all else that one looks for in a collection

REVIEWS OF BOOKS

such as the one under review, and moreover has found, in certain analogous publications which come from less happy shores than ours.

The Physical Society has begun a good work, and we are grateful. We should be still more grateful if, encouraged by a good reception of the Report for 1934, we may hope for a dose both heavier and yet more rarified to record the progress of 1935.

F.I.G.R.

**Spectroscopy (Emission and Absorption Spectra, Electromagneto-optics, Raman Effect, etc.).** Extracted from Vol. X. (1930) of the *Annual Tables of Constants* (A.T.C.), by P. Auger (Paris), L. Bruninghaus (Paris), V. Henri (Liège), and F. Wolfers (Alger). (Pp. 310, 22 cm. × 28 cm. Price, bound, £2—$10. Editor: International Committee of Annual Tables of Constants (A.T.C.), 9 rue de Bagneux, Paris VI°.)

This the tenth volume of Dr. C. Marie's *Annual Tables of Constants* is for the year 1930 and follows in plan Volumes VIII. for 1927-28 and IX. for 1929 which were published together and reviewed in these *Transactions* (Vol. 30, p. 373, 1933). The same plan of arrangement is followed and most of the features described in that review appear. Of these may be mentioned the ease in tracing a subject by its name or author.

As before, the main divisions are: emission spectra, absorption spectra, electro-magnetic optical data, and the scattering of light.

As an example of emission spectra the important one of the iron arc may be mentioned: a list is given of the frequencies of over 3000 lines together with their structure. In this part are treated: atomic spectra (143 pages), molecular spectra (51 pages), and data on resonance, fluorescence and phosphorescence.

Absorption spectra of gases, liquids and solids in the ultra-violet and infra-red regions of the spectrum occupy 37 pages and the spectra are freely illustrated as in the previous volume by reproductions of the authors' curves.

As before, a useful list is given of the data published during the year on the different " effects," such as that of Stark, Zeeman and Cotton. Apart from a few data on the ordinary scattering of light, this section is occupied with examples of the Raman effect in solids, liquids, solutions and gases, and includes data on the intensity and polarisation of the Raman scattered line.

The sectional editors, Auger, Bruninghaus, Henri and Wolfers deserve our gratitute for this complete and useful compilation.

R. R.

ABERDEEN: THE UNIVERSITY PRESS

# CONDUCTIVITY-TEMPERATURE STUDIES ON PARAFFIN WAXES.

By W. Jackson, M.Sc., A.M.I.E.E., *Magdalen College, Oxford.*

Although a large amount of information is available,[1] the behaviour of dielectric materials under direct electric stress is not well understood, even in the case of highly purified simple liquids. For the more complex hydrocarbon liquids and for solid materials little is known of the source and nature of the charge carriers and of the mechanism of their accumulation and discharge at the electrode surfaces. However, it has appeared general for the residual D.C. conductivity to increase continuously, though not necessarily uniformly, with increase in temperature. This characteristic may be accounted for in the increasing number of ions available due to greater dissociation and in the reduction of the viscous resistance to ionic movement. Previous to the publication of a letter[2] of which the present paper is a development, the only recorded exception to this behaviour appears to have been by Gemant.[3] He observed that while the residual conductivity of a heavy cable oil increased with temperature from $-60$ to $-35°$ C., it decreased between $-35$ and $-15°$ C.; beyond the latter point it increased continuously. This form of variation of conductivity with temperature has been observed in a number of different samples of paraffin wax, and the temperature region in which it is found suggests that the phenomenon is related closely to the occurrence of a transition in the crystalline structure of the wax.

## Description of the Conductivity Measuring Equipment.

The measurement of the residual D.C. conductivity of materials of good dielectric properties is complicated by the fact that with voltage gradients of desirably low magnitude, and a test condenser of reasonable dimensions, the currents flowing are exceedingly small. It was anticipated that the need would arise to measure specific conductivities of the order of $10^{-18}$ mho/cm., and with the condenser available this called for the determination of resistance values of the order of $10^{13}$ ohms. The most convenient instrument for this purpose is a direct current amplifier, and the circuit diagram of the one developed is shown in Fig. 1.

The valve employed is an " electrometer " triode for which the whole of the energising voltages are provided by an 8-volt battery $E_1$. This drives a common current through the filament, the anode resistance $r_1$, the grid bias resistance $r_2$, a calibration potentiometer resistance $r_3$ (voltage drop, 45 m.v.), and a current adjusting resistance $r_4$. The grid circuit

[1] W. Jackson, *J. Inst. Elec. Eng.,* 1934, **75,** 93.
[2] W. Jackson, *Nature,* 1934, **133,** 647.
[3] A. Gemant, *Z. Physik,* 1932, **75,** 613.

contains two high resistances $R_1$, $R_2$ of $5 \times 10^6$ and $1.45 \times 10^9$ ohms respectively, each of which can be completely isolated at quartz insulated switches $S_1$, $S_2$, and either of which can be connected *via* the switch $S_3$ to form a local circuit with the test condenser $R_x$ and a suitable voltage $E_3$. The current traversing $R_x$ and $R_1$ (or $R_2$) develops a small P.D. across the latter and produces a related change in anode current. The magnitude
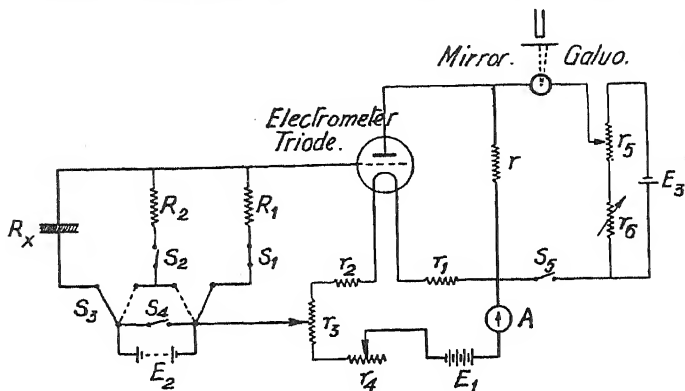


of this P.D., and therefore the value of $R_x$, may be determined either by balancing out the change of anode current by applying an equal, but reverse, voltage change on the potentiometer $r_3$,

FIG. 1.

or by calibrating the anode current change in terms of the calibration of this potentiometer. The normal anode current is balanced in the reflecting galvanometer by use of the combination $r_5$, $r_6$, $E_3$. The resistance $R_1$ is of the grid leak type, but $R_2$ is a sealed liquid resister consisting of a mixture of ethyl alcohol, benzene, phenol and picric acid.

The valve, together with the resistances $R_1$, $R_2$, is mounted in a sealed metal case dried by means of calcium chloride, and the whole circuit, with the exception of the galvanometer and batteries, in a wooden box through which the necessary terminals protrude. All the important leads are brought through quartz tubing in order to ensure the desired high insulation of the valve input circuit. The overall sensitivity of the device is 1·0 cm. galvanometer deflection per 3·0 m.v. change in grid potential.

The condenser and the method of temperature variation employed in the measurements have been described elsewhere in a similar connection.[4] The condenser consists of a shallow metal container of which the base forms one electrode ; the other electrode, a flat disc normally completely immersed in the dielectric under test, is supported on a crown glass plate closing the top of the container. This plate is provided with a guard ring on both its upper and lower surfaces, the two being joined at the stoppered hole through which a thermometer enters the condenser. As an added precaution against error due to leakage across the surface of the glass cover, the test condenser was compared at each temperature with an identical condenser having air dielectric. The insulation resistance of this latter condenser was always too high to be measured, but this fact gave the required assurance of freedom from error due to surface leakage in the similarly situated test condenser.

## Measurements of Residual Conductivity as a Function of Temperature.

The measurements previously recorded [2] related to a sample of paraffin wax (melting-point, 45 to 55° C.) which had been deteriorated by heating in air at 100° C. for several hours. In consequence its specific conductivity was relatively high. On raising the temperature very slowly from 2° C.

[4] W. Jackson, *Proc. Roy. Soc.*, 1933, 142A, 606.

the conductivity increased up to 16° C.; at this point the temperature coefficient became negative until at 34° C. the conductivity passed through a minimum; it then increased at a rapid rate. The curve for decreasing temperature was similar in form and gave a minimum at about the same temperature 34° C. Below this point the conductivity values were much lower than those observed with an increasing temperature, but showed a maximum at about 20° C. Subsequent tests gave curves of the same form, although the actual values of conductivity varied appreciably from test to test.

Attention has since been devoted to paraffin waxes of more defined melting-point. In each case the wax was filtered and then degassed for one hour at 100° C. before it was poured into the condenser. The curves of Fig. 2 were obtained during temperature rise from 2° C. on a paraffin classed as a 57 to 60° C. melting-point wax *; curve (a) relates to the wax alone and curve (b) to a 4·78 per cent. solution of cetyl palmitate in the wax. It is seen that the behaviour in both cases is similar to that described above. The effect of the cetyl palmitate addition is to increase the conductivity appreciably, but of more interest is the fact that the position of the minimum in the conductivity-temperature curve is depressed from 42 to 40° C. Although the general form of these curves was reproducible, and the positions of the maximum and minimum recurred at temperatures within about ± 1° C. of those indicated in Fig. 2, the actual
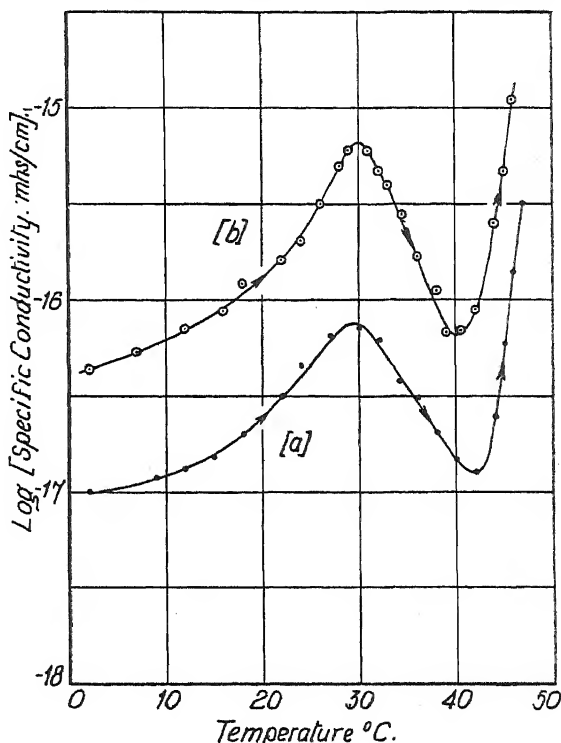


FIG. 2.

conductivity values did not repeat on repetition of the test. It was clear that the conductivity of the wax in the solid state at a given temperature is markedly dependent on its previous history. This is demonstrated in the curves of Fig. 3 relating to a vacuum fractionated wax of melting-point 55° C. which had been twice recrystallised from benzene.† The measurements in this case were made with falling temperature; for curve (a) the wax was raised to a temperature of 50° C. and then allowed to cool at the rate of about 6° C. per hour; for curve (b) the temperature was raised well beyond the melting-point before measurements were commenced.

The former curve is noteworthy because of the sudden drop in conductivity at 40° C.; near this temperature there was a noticeable halt

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* Supplied by the Shell Mex Company.
† Supplied by the Burmah Oil Company.

in the rate of temperature fall.    No arrest of temperature fall was apparent for curve (b) where the behaviour was similar to that experienced with the previously menti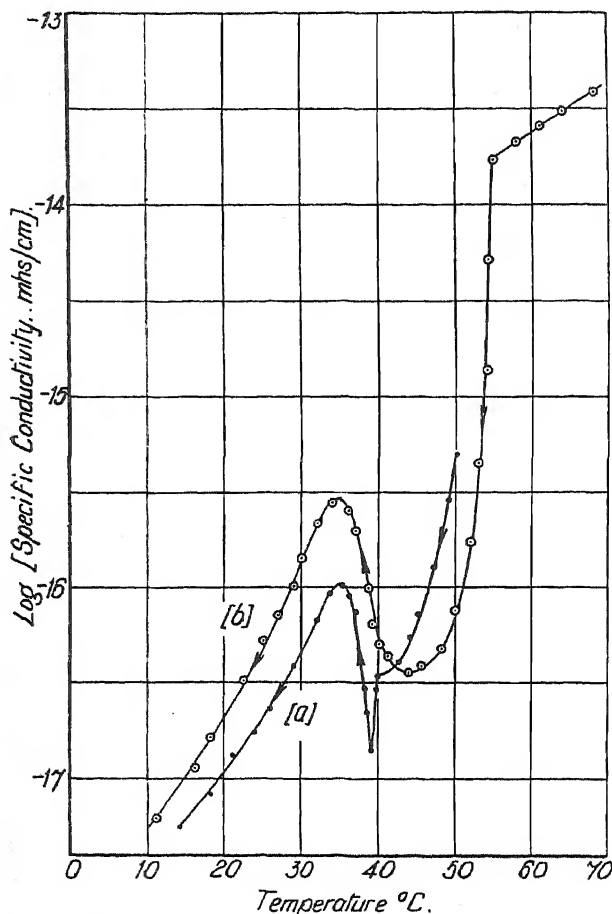oned waxes.    Curve (b), Fig. 3, is of particular interest because it demonstrates the effect of the commencement of solidification on the conductivity. The molten material shows a normal decrease of conductivity with temperature, but following the advent of crystallisation the temperature remained sensibly constant for a long period, and during this period the conductivity decreased very rapidly.



FIG. 3.

## Dielectric Absorption as a Function of Temperature.

In measuring the residual conductivity the voltage was applied continuously across the test condenser. This residual conducting state was attained, however, only after several minutes voltage application, and during this interval an anomalous charging current was observed to flow. Analogously, on short circuiting the charged condenser through the relatively low resistance $R_1$ at the switch $S_4$, its discharge lasted for several minutes in a manner characteristic of dielectric absorption. The variation of this discharge current with time could be followed on the anode circuit galvanometer beyond about five seconds of the instant of short circuit. As is usual in time studies of dielectric absorption, the discharge could not be represented by a simple exponential relation, and attention is directed only to the character of the current at instants close to that of short circuit. In investigating the effect on this of temperature variation, the charging voltage was applied at each observation for a constant period of five minutes.

Each of the wax samples tested in this manner showed the same general behaviour, so that it is sufficient to record the results obtained on the sample of 57 to 60° C. melting-point wax containing 4·78 per cent. cety

palmitate.   The value of the discharge current at ten seconds after the
short circuit of this medium, taken per unit voltage applied during charge,
is shown plotted against the temperature in Fig. 4.   It is seen that the dis-
charge current
value at this
instant passes
through a maxi-
mum in the
region of 24° C.
In Fig. 5 the
time constant of
the discharge be-
tween ten and
twenty seconds,
derived on the
assumption of a
simple expon-
ential decay be-
tween these in-
stants, is plotted
also on a function
of temperature.
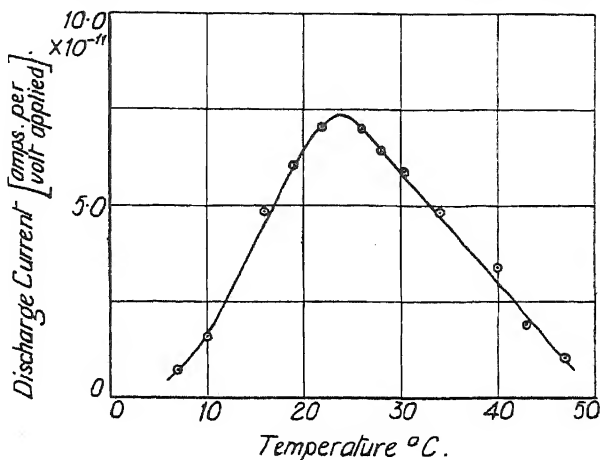This equivalent
time constant is
of the order of



FIG. 4.

several seconds, and is observed to decrease continuously with rise in the
temperature in a quite normal manner.   Beyond 50° C. the discharge
became of too short duration to permit of reliable measurements.

The theories of dielectric absorption fall into two classes ; those which
regard the absorption current as due to the restricted movement of ions
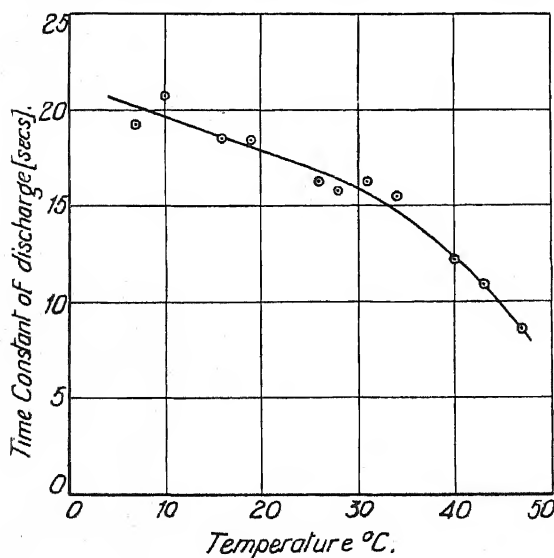and those concerned with the orientation of dipole molecules or aggregates.[1]



FIG. 5.

Before discussing the
results given in Figs.
4 and 5, it is im-
portant, therefore, to
identify them with
one or other type of
absorption mechan-
ism.  Any absorption
effect, being perfectly
reversible, must be
responsible for power
loss when an alter-
nating electric field
is applied, and the
power loss per cycle,
or the power factor,
passes through a
maximum with vari-
ation of either tem-
perature or frequency
when the conditions
are such that $\omega\tau = 1$
(very approximately).
Here $\tau$ is the time
constant, or relaxa-
tion time, of the

relevant absorption mechanism, and $\omega = 2\pi \times$ frequency (c.p.s.).   Fig. 6
shows the variation of power factor with temperature at each of four
constant frequencies for the 4·78 per cent. cetyl palmitate-paraffin wax

solution to which curve (b), Fig. 2, and Figs. 4 and 5 refer. The cetyl palmitate molecule is polar, and this power factor has been identified with the viscous orientation of its polar group in the surrounding wax medium.[5] It is seen that the time constant of this orientation at 20° C. is of the
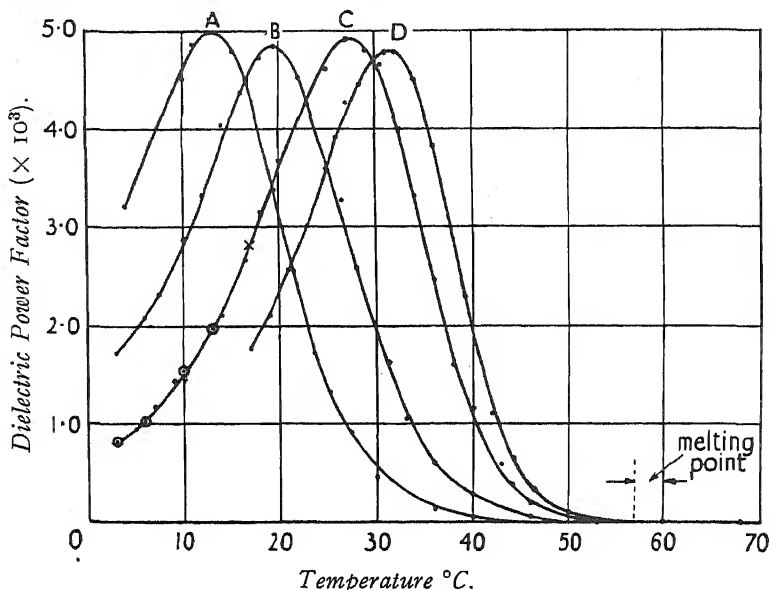


Fig. 6.

order of $10^{-8}$ second. The absorption currents dealt with in Figs. 4 and 5 cannot arise, therefore, from this source, and it may be concluded in consequence that they are to be accounted for on an ionic basis.

## Discussion of the Observed Effects.

As previously mentioned, the phenomenon depicted in the curves of Figs. 2 and 3 was first observed in measurements on a paraffin wax of quite undefined melting-point, and at the time of the original communication it seemed reasonable to suggest that its appearance was concerned with the probable presence in the wax, at temperatures below the solidifying-point, of two phases, a solid crystalline network and an interspersed liquid, or amorphous, phase. Gemant has employed this sort of conception in a recent discussion [6] of the analogous results he obtained in low temperature measurements on a heavy cable oil. The crystalline phase is regarded as having a greater characteristic conductivity than the amorphous phase, and his analysis consists in deriving the manner in which the relative proportions of these constituent phases must vary with temperature in order to provide a conductivity variation for the mixture corresponding to that observed experimentally. This conception is not inappropriate even for the refined waxes to which attention is drawn in the present paper, but it now seems probable that the changes in the residual conductivity of the wax with temperature arise from the occurrence of a transition in the crystalline structure at a point somewhat below the temperature of solidification.

[5] W. Jackson, *Proc. Roy. Soc.*, 1935, A. In print.
[6] A. Gemant, *Nature*, 1935. In print.

In a series of observations on the cooling of paraffin waxes in mass, and of their crystallisation from organic solvents, J. A. Carpenter [7] has shown the existence of a transition-point between two crystalline forms at a temperature some 10 to 15° C. below the melting-point. Above this transition the crystals are stated to be needle-shaped prisms, while below it they take the form of rhomboid plates or leafy masses.

More definite information concerning the position of this transition-point has since been supplied in the work of A. Müller [8] on highly-refined paraffins. As the number of carbon atoms in the paraffin molecule is increased from 26 to 44, with continuous increase in the melting-point from 58 to 86·4° C., he has shown that the distance of the transition-point below the melting temperature decreases from 12 to 0·5° C. The Burmah Oil Company have given the transition-point of the wax supplied by them, Fig. 3, as 41·7° C., that is 13·7° C. below the stated setting-point of 55·4° C. This figure compares well with Müller's results, and it is probable that further recrystallisation of the fraction tested would have led to still closer agreement.

On examination of curve (a), Fig. 2, it is seen that the conductivity passes through a minimum at about 42° C., that is at 15° C. below the solidifying-point. Moreover, the addition of cetyl palmitate to the wax



FIG. 7.

causes a depression of this minimum point by about 2° C., curve (b), in a manner to be expected from transition-point considerations. Similar deductions result from examination of Fig. 3, since in curve (a) the sudden drop in conductivity at 40° C. occurs 15° C. below the setting-point, and the conductivity minimum of curve (b) appears at about 11° C. below the latter point.

On the basis of these observations it seems probable that the ideal curve of a pure hydrocarbon would be of the form ABCDE, or ABB'CDE, Fig. 7. Here B represents the solidification and C the transition-point. The waxes studied were quite certainly composed of a variety of hydrocarbons of slightly different melting-point, so that it is not to be expected that the transition-point of the mixture will be well defined. This may well account for the somewhat gradual transfer from the
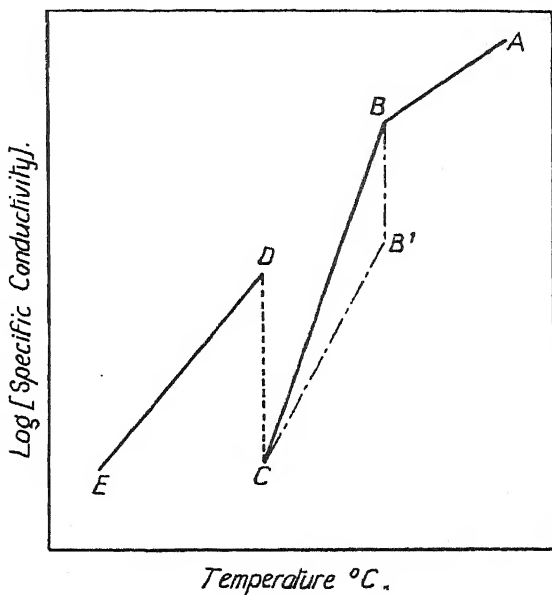
[7] J. A. Carpenter, *J. Inst. Petr. Techn.*, 1926, **12**, 288.
[8] A. Müller, *Proc. Roy. Soc.*, 1932, **138A**, 514.

hypothetical curve BC, or BB'C, to curve DE apparent in the experimental results. It is significant that the temperature separation between the maximum and minimum points of the conductivity curves appears to decrease as the definition of the melting-point increases; thus it was $17°$ C. for the wax in which the effect was first observed,[2] $13°$ C. for the 57 to $60°$ C. melting-point wax, curve $(a)$, Fig. 2, and $10°$ C. for the still more refined wax of curve $(b)$, Fig. 3. In curve $(a)$, Fig. 3, relating to the latter wax, the separation is only $4°$ C.

The presence in the wax of a variety of constituent hydrocarbons, and the occurrence of structural changes with temperature variation, at once introduces the possibility of dielectric absorption of the type dealt with by the Maxwell-Wagner theory.[1] It remains only to explain the passage of the instantaneous absorption current through a temperature maximum as shown in Fig. 4. The possibility of this follows, however, on the assumption of certain, normally correct, modes of variation of the relevant quantities. Thus let the absorption current be represented as a function of time in the form

$$i(t) = E\sigma e^{-t/\tau}$$

where $\sigma$ is the initial conductivity and $\tau$ the appropriate time constant. Further, let the conductivity vary with absolute temperature $T$ according to the relation

$$\sigma = \sigma_0 e^{-\alpha/T}$$

and the time constant $\tau$ follow a variation with temperature analogous to the normal viscosity variation

$$\tau = \tau_0 e^{\beta/T}.$$

Then $i(t)$ may be written

$$i(t) = E\sigma_0 e^{-\left\{\frac{\alpha}{T} + \frac{t}{\tau_0} \cdot e^{-\beta/T}\right\}}.$$

For a given value of the time $t$, $i(t)$ passes through a maximum at a temperature $T$ for which $\frac{d}{dT}[i(t)] = 0$, and this occurs when

$$T = \frac{\beta}{\log \frac{\beta}{\alpha} \cdot \frac{t}{\tau_0}}.$$

Although the above relations cannot justifiably be taken to hold in the present instance, it is not unlikely that the general principle enumerated is applicable.

## Summary.

It has appeared characteristic of dielectric materials that their residual D.C. conductivity should increase continuously, though not necessarily uniformly, with increase in temperature. Measurements on a number of different samples of paraffin wax have shown, however, that the conductivity has a negative temperature coefficient over a limited range of temperature terminating some 10 to $15°$ C. below the melting-point. Purified hydrocarbons of comparable melting-point are known to undergo a transition in crystalline structure at about $12°$ C. below this temperature, and the observed changes in conductivity with temperature are apparently

due to such a transition. It was also observed that the instantaneous absorption circuit in the waxes passed through a maximum with temperature, and this is explained tentatively in terms of normal variations of the relevant physical factors.

# ON THE MECHANISM OF EMULSIFICATION BY ULTRASONIC WAVES.

By C. Bondy and K. Söllner.

It has been known since the work of Wood and Loomis,[1] that ultrasonic waves readily bring about the formation of emulsions in two-liquid systems such as water/oil (the term oil is used for organic liquids not miscible with water) or water/mercury. The mechanism of this emulsification has been investigated more than once and theoretical explanations have been advanced to account for it.[2] But since there is apparently as yet no really satisfactory theory, it seemed worth while to attack the problem again.[3]

Experimental results, which will be discussed later, led us to the conclusion that there is a fundamental difference in the mechanism leading to the formation of emulsions in water/oil and water/mercury systems. This paper deals only with the former type of emulsions, mercury emulsions being discussed in the following paper.

We further came to the conclusion that a so-called *cavitation* at the interface causes emulsification.

In the literature on ultrasonics the term " cavitation " has been used by several writers when merely referring specially to the expulsion of dissolved gases.[4] We found it necessary to revert to its original meaning as known in hydrodynamics. Since cavitation and the phenomena correlated with it are not generally known, an introductory note will deal with them.

[1] R. W. Wood and A. L. Loomis, *Phil. Mag.* (7), 1927, **4**, 417.
[2] W. T. Richards, *J. Am. Chem. Soc.*, 1929, **51**, 1724. E. N. Harvey, *Biol. Bull.*, 1930, **59**, 306. N. Marinesco, *Compt. rend.*, 1933, **196**, 346. F. Rogowski and K. Söllner, *Z. physik. Chem.* (A.), 1933, **166**, 428.
[3] The apparatus used for this work was described by H. Freundlich, F. Rogowski and K. Söllner, *Kollch. Beih.*, 1933, **37**, 223 ; *see also* the same authors, *Z. physik. Chem.* (A.), 1932, **160**, 469.
[4] W. T. Richards and A. L. Loomis, *J. Am. Chem. Soc.*, 1927, **49**, 3086. F. O. Schmitt, C. H. Johnson, and A. R. Olson, *ibid.*, 1929, **51**, 370. C. H. Johnson, *J. Physiol.*, 1929, **67**, 356. E. N. Harvey, *loc. cit.*[2].

29 *

## The Formation of Cavities in Liquids.

The word "cavitation" was introduced (in 1894) when engineers first [5] became acquainted with high speed propellers and steam turbines and were, thus, obliged to take into account "cavitations" produced by the rapid rotation.

Cavitation can occur as soon as the hydrodynamical pressure in a liquid is reduced to the vapour pressure.[6] Where this is the case the liquid may disrupt and so be transformed into a two-phase system, containing a fluid and a gaseous phase. This disruption is somewhat analogous to the disruption of stretched liquids in the experiments of M. Berthelot,[7] Worthington and J. Meyer.[8] These will always be referred to as the experiment of Berthelot. Now in these cases the liquid does not disrupt under well-defined conditions ; the phenomenon is largely dependent upon fortuitous circumstances. It is commonly known, for instance, that stretched fluids are very sensitive to feeble shocks and furthermore that it is absolutely essential to remove all nuclei of gases. Impurities likewise have a marked influence on the tensile strength of liquids. The theoretical values, as calculated from van der Waals' equation, have never been realised, the maximum stretches found experimentally amounting only to a few per cent. of those theoretically possible. From this fact it is to be concluded that there are always "loose-spaces" ("*Lockerstellen*") present in a liquid. It is probable that dissolved gases are instrumental in the formation of such "loose-spaces." If a liquid, saturated with gas, is stretched, a gas nucleus may be formed which can act as a "loose-space" and so lead to the disruption of the fluid, provided that it is stretched to a sufficient extent.

Osborne Reynolds [9] described a very impressive experiment demonstrating the formation of cavities in a streaming liquid. Water, allowed to stream through a convergent—divergent tube (see Fig. 1), turns opaque at the narrowest constriction (of the tube), if the rate of flow exceeds a certain minimum



FIG. 1.

value. The zone of opacity extends for some millimetres down stream. At the same time a loud hissing noise is heard ; Osborne Reynolds calls this phenomenon "the boiling of water in an open tube at ordinary temperature" and points out that the hissing sound arises from the same cause (*i.e.*, the collapse of cavities) as the singing of a kettle shortly before the water boils. In both cases, the hissing is caused by the condensation of steam bubbles passing into regions of higher pressure or lower temperature respectively.

This experiment of Reynolds can readily be repeated by connecting to the water mains a not too narrow glass tube drawn down in the middle to about 1 mm. inside diameter.

[5] The possibility of the formation of cavities was discussed by L. Euler as far back as 1754 in his *Theorie plus complète des machines, qui sont mises en mouvement par la rèaction de l'eau*. A general account of cavitation is given in *Hydraulische Probleme*, V. D. I. Verlag, Berlin, 1926, and H. Mueller, *Naturwissenschaften*, 1928, **16**, 423.

[6] It is not known, as yet, whether this is also true for absolutely pure and gas-free liquids.

[7] M. Berthelot, *Ann. Physique et Chim.* (3), 1850, **30**, 232.

[8] A. M. Worthington, *Phil. Trans.*, 1892, **183A**, 355 ; *Proc. Roy. Soc.*, 1892, **50**, 423. J. Meyer, *Zur Kenntnis des negativen Drucks in Flüssigkeiten, Abhandlungen d. Deutsch. Bunsengesellschaft*, Nr. 6 (1911).

[9] Osborne Reynolds, *Papers on Mechanical and Physical Subjects*, Cambridge, 1901, **2**, 578.

The cavitation in such a tube is easily understood. According to Bernoulli's equation

$$P + \frac{\rho v^2}{2} = constant.$$

($P$ being the hydrodynamical pressure, $\rho$ the density and $v$ the velocity), the sum of pressure and kinetic energy in a flowing liquid is a constant. Thus the velocity of a liquid passing through a restriction may become so high that the hydrodynamical pressure is reduced to the vapour tension.

According to Reynolds the presence of dissolved air exerts a distinct influence. In liquids which, like tap water, contain a sufficient amount of dissolved air, cavitation is always accompanied by partial de-gassing.[10] This may be explained by the fact that minute gas bubbles are formed where the liquid disrupts. These bubbles quickly unite to larger ones, which are not so readily redissolved in regions of higher pressure.

### The Collapse of Cavities.

One effect brought about by the collapse of cavities has already been mentioned, viz. the singing of a kettle. Cavities collapse, as soon as the conditions which have led to their formation cease to exist. In most cases decavitation, so to speak, is due to rising pressure or decreasing temperature in the surrounding liquid.

The investigations of Reynolds inspired the late Lord Rayleigh to calculate the pressure developed during the collapse of a spherical cavity.[11] The result of his derivation is given by the equation :

$$\frac{P'^2}{2\beta} = \frac{P}{3}\left(\frac{R_0^3}{R^3} - 1\right).$$

($P$ being the pressure at infinity external atmospheric pressure ; $R_0$ the initial radius of the cavity ; $\beta$ the coefficient of compressibility ; $P'$ and $R$ being the correlated pressure and radius of the cavity during the collapse.)

Calculation shows that pressures of thousands of atmospheres may be developed at the moment when the cavity collapses to a small fraction of its original diameter. Obviously such collapses may cause enormous mechanical effects, high kinetic energies being concentrated at very small spots. In fact, mechanical engineering and, specially, naval construction are quite familiar with effects of this kind. The mechanical impact due to decavitation produces extremely heavy erosion, which can be distinguished from ordinary corrosion by its different appearances and by the places where it occurs. These places moreover may be predicted from hydrodynamical reasoning. Föttinger,[12] who advanced this theory of erosion by cavitation, was able to prove his views by showing that glass, which is chemically inert, is also attacked under corresponding conditions. To give some impression of the amazing effects of cavitation, it may be mentioned that after a destroyer had rushed for several hours at maximum speed, the armour plates above the propeller were pierced by a hole of the dimensions of about one square foot. Likewise turbines may be strongly attacked during short runs.[13]

[10] O. Reynolds describes this phenomenon as follows : " When the hiss is on, the water in the tube will be somewhat opaque—rather foggy—which fog disappears after the hiss is stopped. This fog is caused by the separation of the air occluded in the water and corresponds exactly to the separation of the air, as when the temperature of the water in the kettle is above $174°$ F. In the case of the tube the bubbles of air, which separate out, are very much smaller than those in the kettle on account of the greater violence of the action."

[11] Lord Rayleigh, *Phil. Mag.* (6), 1917, 34, 94.

[12] H. Föttinger, *Hydraulische Probleme, loc. cit.*,[5] p. 14.

[13] Apart from these mechanical effects, chemical effects of cavitation must also be assumed according to H. Föttinger, *loc. cit.*,[5] who points out, that owing

It will be apparent therefore that strong mechanical action may arise from cavitation.    Now, we hope to show that intense ultrasonic waves are able to produce this phenomenon, and furthermore that emulsification under their influence only takes place when there is a chance for the formation, as well as for the collapse, of cavities in the radiated system.

## Emulsification Caused by the Collapse of Steam Bubbles.

We will first prove that the collapse of cavities does indeed represent a most efficient method for dispersing systems of water and oil.

Probably the simplest way of producing cavities is to let steam condense in its own liquid phase, as in the case of the singing kettle.    If for instance steam from boiling water—or even better, superheated steam —is brought through a nozzle of about 1 mm. diameter into the interface of water and oil, it condenses with the well-known rattling noise, a highly dispersed emulsion of the O/W type being formed at the same time.    When using a soap solution instead of pure water, concentrated emulsions may be produced, provided the experiment is continued long enough.    It is evident that this experiment is fundamentally different from all those where an emulsion is obtained when the steam of the *disperse* phase is introduced into the cool medium of dispersion.    The fact that emulsification ceases as soon as the water becomes too warm to allow of sufficiently rapid condensation proves that in our case the collapse of cavities is essential.    If air, instead of steam, was blown into the system, there was no effect whatsoever, in agreement with what was to be expected.    On the contrary the addition of air to the steam reduces its efficiency, since the gas buffers the impact of the collapsing steam bubbles.    The method of dispersing organic liquids in water by means of steam turned out to be of quite general value when producing all sorts of emulsions.

## Cavitation Caused by Acoustic Waves.

How far may ultrasonic and also acoustic waves give rise to similar effects ?    Since sound waves consist of periodical compressions and expansions, it seems quite legitimate to suppose that, provided the energy is sufficiently high, cavities may be formed in a liquid during the expansion phase.    Some sixty years ago it was shown that acoustic waves are able to disrupt a fluid.    Kundt and Lehmann [14] in their well-known paper on dust figures and velocities of sound in liquids describe an interesting experiment as follows :

" If a tube was completely filled with water which had not been de-gassed, but from which all—even the smallest—bubbles had been removed, and was set into vibration by strongly rubbing the glass rod, air bubbles were formed which grew markedly when the vibration continued.    This is able to drive the dissolved air out of the water. The air bubbles disappear again, *i.e.*, the air is absorbed, if the experiments are stopped for some time."

Even more conclusive is the following observation of Kundt and Lehmann, which was made with a carefully de-gassed fluid :    " While the whole system was vibrating vehemently we several times noticed

to locally developed high pressures and temperatures and to the possibility of ballo-electric phenomena the occurrence of oxidations, dissociations, etc., is to be expected.

[14] A. Kundt and O. Lehmann, *Ann. Physik*, [*Pogg.*), 1874, **153**, 1.

that the water close to the end of the vibrating rod turned turbid. Since it was entirely free from air, these small bubbles causing the turbidity could only be due to the disruption of the water (*Zerreissen in kleine Partien*) under the influence of these intense vibrations."

This is evidently the same phenomenon as the formation of cavities in Reynolds' experiment mentioned above.

Kundt and Lehmann's experiments definitely show that acoustic waves may cause cavitation in de-gassed liquids and the expulsion of dissolved gas in gas-containing liquids.

## Cavitation Caused by Ultrasonic Waves.

In these circumstances one need not hesitate to assume that intense ultrasonic vibrations may also cause cavitation. The following facts confirm this assumption :

1. Hopwood showed that liquids having a low boiling-point may be made to distil at room temperature when radiated by ultrasonics.[15] This agrees with the fact described by Richards and Loomis [16] that ultrasonics lower the boiling-point.

2. The ability of ultrasonics to evolve gas from gas-containing liquids.[17]

3. The fact [18] that liquids stretched according to Berthelot's method (*i.e.*, liquids cooled down slowly after having been sealed into a tube at higher temperatures) are disrupted at a higher temperature, *i.e.*, at a feebler static stress, when exposed to ultrasonics.

The formation of cavities seems to be favoured at interfaces. This may be correlated to the fact, already emphasised by Wood and Loomis, that ultrasonics are specially active at interfaces (heat effects, etc.). It can be seen from an experiment of Freundlich and Lindau that cavities tend to appear at the interface of two liquids. If water, in a Berthelot experiment, is stretched in a tube which also contains mercury, bubbles appear notably at the interface water/mercury, when the liquid disrupts. When an oil-wetted tube is used, many small bubbles are formed at the wall on disrupting, whereas only one bubble appears, when the walls of the tube have been wetted with water. The most direct evidence is that, when radiating a two-phase system with ultrasonics the formation of gas bubbles is seen to be most pronounced at the interface.

## Emulsification by Ultrasonics.

When applying these results to the question of emulsification the following assertion has to be proved : emulsions are only obtained when the conditions are such that cavities are not only produced but also collapse. Their formation alone does not give rise to any remarkable

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[15] F. L. Hopwood, *Nature*, 1931, **128, 748**. This reminds of the remark of O. Reynolds quoted above : " The boiling of water in an open tube at ordinary temperature."

[16] Richards and Loomis, *loc. cit.*[4]

[17] It is important to remark that de-gassing does not implicitly require cavitation. Expansions, many times smaller than those necessary for cavitation, are sufficient to cause bubbling in gas-containing fluids. This was first emphasised by R. W. Boyle and G. B. Taylor, *Physic. Rev.* (2), 1926, **27,** 518.

[18] Unpublished experiments of H. Freundlich and G. Lindau. This typical example may be mentioned : de-gassed water, sealed into a tube at 43° C. disrupts at 31° C., if cooled down in the usual way, it already disrupts at 36° C. if radiated by ultrasonics.

effects. Liquids radiated *in vacuo* with ultrasonics practically only boil. Cavities are formed, but they do not collapse [19] because the vapour pressure in the cavities is practically in equilibrium with the pressure outside. Now, Rogowski and Söllner [20] have already found that the presence of gas is essential for emulsifying by means of ultrasonics. Pairs of liquids, such as water/paraffin, oil, or water/toluene, carefully freed from gas and sealed in an evacuated tube are not emulsified. Nor are emulsions formed *in vacuo* even in the presence of efficient stabilisers such as sodium oleate. This proved that the presence of gases is instrumental for the mechanism of emulsification.

If the liquids are sealed under gases at atmospheric pressure (no matter whether they be air, $N_2$, $O_2$, $H_2$, Ar, He), the liquids being saturated with the gas, they are easily emulsified by ultrasonic radiation. These facts were found to hold for a great number of organic liquids. If the liquids are exposed to a certain external pressure, the cavities collapse and emulsification takes place.

This behaviour was investigated more quantitatively. It could be shown experimentally that a certain value of external pressure is essential to render cavitation efficient. The emulsification of toluene in water was studied at different air pressures, the liquids being always in equilibrium with the gas. The experiments with pressures smaller than atmospheric were done in sealed tubes, the others in open tubes of exactly the same shape, the latter being connected to a compressed air cylinder. When comparing the resulting emulsions of toluene in water, it was evident that a high concentration was not reached until the pressure exceeded a value of about 100 mm. Hg; then, there is a broad range where the concentration increases with increasing pressure. At still higher pressures, above about 2 atmospheres, emulsification decreases again. Table I. contains the results.

TABLE I.

| Pressure in mm. Hg. | Disperse Phase (after 30 sec.) in Per Cent. |
|---|---|
| 00 | 0·0 |
| 60 | 0·0 |
| 100 | 0·3 |
| 150 | 1·0 |
| 200 | 2·6 |
| 300 | 3·2 |
| 600 | 4·1 |
| 760 | 4·4 |
| 1100 | 5·0 |
| 1500 | 5·7 |
| 2300 | 4·1 |
| 4000 | 1·2 |

The concentration of the emulsion was determined by measuring the densities by means of a pyknometer.

A formation of bubbles was always observed.

The differences found can only be explained by assuming that the cavities collapse with different vehemence. The decrease in efficiency at high pressures—the liquids were always saturated with air—may be partially due to the fact that the formation of cavities is rendered more difficult, partially to the fact that the cavities contain too much gas if formed in a solution with a high gas concentration. The gas then

[19] R. W. Boyle and G. B. Taylor, *loc. cit.*[17] express the same fact, when saying that the sound energy transmissible per sq. cm. through a liquid is limited by a phenomenon of cavitation according to the expression :

$$E = \frac{(p - p_v)^2}{2\rho c}$$

($E$ being the transmissible energy, $p$ the hydrostatic pressure, $p_v$ the vapour pressure of the liquid, $\rho$ its density and $c$ the velocity of sound in the radiated medium.)

[20] F. Rogowski and K. Söllner, *loc. cit.*[2]

acts again as a buffer, as was the case in the experiments done with steam.[21]

There is yet another most important similarity to the dispersing action of steam : emulsification by ultrasonics is much feebler when hot liquids are used. This is quite contrary to the usual experience in the technique of emulsification. It is hard to imagine any other mechanism in which emulsification would be decreased by a rise in temperature. All kinds of stirring effects, as assumed by some previous authors, should be improved at higher temperatures.

Some details as to the formation of cavities by ultrasonic waves also deserve further consideration. When discussing the experiments of Berthelot and Osborne Reynolds, it was emphasised that the disruption of liquids largely depends upon a ready production of nuclei from dissolved gases. As was to be expected, a similar influence is found with ultrasonics : pairs of liquids such as water/benzene or water/nitrobenzene—saturated with gas at atmospheric pressure—were radiated at higher hydrostatic pressures.[22] The liquids were contained in long tubes (about 25 cm.) of 10 mm. diameter. The amount of the heavier liquid was so small that its height was not more than 2·5 cm., while the lighter liquid practically filled the rest of the tube. Pressure was provided by a compressed-air cylinder. As the pressure increased emulsification rapidly decreased, and no emulsion was obtained when the pressure exceeded a certain value. This value depends on the ultrasonic energy, the temperature and the liquids used. A hydrostatic pressure of several hundred mm. Hg exerted a decisive influence.[23] This behaviour was not changed by stabilisers such as soaps or gelatin. Control experiments at normal pressure always showed strong emulsification.

This result may be explained as follows : when hydrostatic pressure is applied, the system is no longer saturated as to the gas, the high column of liquid preventing saturation. Nuclei, which might have been present, are dissolved and conditions are unfavourable for the production of new ones. Consequently no cavities are formed and emulsification is prevented. It is evident that for this reason also, the liquids are not de-gassed under these conditions.

Another point needs discussion. The stretching of a liquid in the experiments of Berthelot is different from that caused by ultrasonic waves, in so far as, in the former case, the liquid only undergoes a static stress, whereas ultrasonic cause a stress varying with the period of the vibration, thus causing strong movement. The latter circumstance evidently favours disruption. This is also borne out by the fact that in Berthelot's experiment the stretched liquid is sensitive towards gentle shocks.

We leave undecided the exact mechanism of this process, there being involved the extremely difficult problem of the formation of primary nuclei and their size.

[21] This buffering action is perhaps also the reason why a certain time of initiation must elapse before strong emulsification begins.

[22] Experiments, mainly biological, with pressures both lower and higher than atmospheric have already been carried out by several authors : F. O. Schmitt, C. H. Johnson and A. R. Olson, C. H. Johnson, E. N. Harvey, *loc. cit.*[4]

[23] It is well known that cavitation can be prevented by an external pressure. Engineers make use of this fact by applying hydrostatic pressures to pumps and turbines and by designing propellers of ships to operate at the lowest possible position below the water level.

The influence of gases is so important and so complicated that it seems advisable to summarise all effects discussed here.

**I. Dissolved gases** may *favour* emulsification, because they favour the formation of nuclei and thus of cavities :

*At higher concentrations* they may be unfavourable to the production of emulsification, because they have a buffering effect upon the collapse of cavities.

**II. An (external) hydrostatic pressure** may be exerted by gases and thus they may exert an influence.

Pressure may *favour* emulsification, because it is necessary for causing an efficient collapse.

A *higher pressure* may be *unfavourable* to emulsification :—

1. If equilibrium is attained, because the energy of the ultrasonics applied can only overcome a certain pressure when forming cavities ;

2. If there is an over-pressure, not in equilibrium with the gas in solution :—

(*a*) Because over-pressure disfavours the formation of nuclei at the interface and therefore the production of cavities ;

(*b*) for the same reason as mentioned under II, 1.

Ultrasonics do not reveal any peculiarities as to the ease of emulsification, apart from the fact that emulsification is favoured at low temperature ; the properties of the emulsions formed are also the same as those of emulsions produced by the usual methods. Ultrasonics, nevertheless represent a very convenient, and efficient, method of preparing protected and unprotected emulsions under clean and reproducible conditions.

We are inclined to believe that many of the destructive effects of ultrasonic vibrations upon living cells as described by biologists [24] are based on the same mechanism as emulsification, *i.e.*, on the collapse of cavities.[25]

## Summary.

1. The emulsifying action of ultrasonic waves in oil/water systems is due to cavitation. Emulsification occurs when cavities collapse.

2. It is shown that cavitation can be caused by sound waves and ultrasonics.

3. The influence of gases upon cavitation is complex. Dissolved gases as nuclei favour the formation of cavities. The hydrostatic pressure exerted by gases is necessary for the collapse of cavities.

4. A new and general method for the preparation of emulsions based on the collapse of cavities was found : the sudden condensation of vapours, such as steam, at the interface of two immiscible liquids rapidly causes strong emulsification.

[24] R. W. Wood and A. L. Loomis, *loc. cit.*,[1] C. H. Johnson, *loc. cit.*,[4] E. N. Harvey, *loc. cit.*[4] (which see [3] for further references).

[25] It does not seem improbable that the chemical effects of ultrasonic waves can be explained in the same way, as was assumed by H. Föttinger, *loc. cit.*[13] for chemical effects of cavitation in general.

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# THE INFLUENCE OF GASES ON MERCURY EMULSIONS PREPARED BY ULTRASONIC WAVES.

By C. Bondy and K. Söllner.

In the preceding paper the mechanism of emulsification in Oil/Water Systems has been discussed. As it was found that mercury is dispersed in water and organic liquids in quite a different manner, the emulsification of metals had to be treated separately.

A gas influence was observed here also.[1] But whereas gases are, with oil emulsions, instrumental for their formation, they seem to have only a stabilising effect with mercury emulsions.

These are the experimental facts : In the absence of gases the amount of mercury dispersed in water by ultrasonic waves is very small. Emulsions, if produced at all, are entirely unstable ; after a short time the water is quite clear again, all the disperse phase having settled down and united with the bulk mass, which then shows its normal reflecting surface. Where gases are present (air, $N_2$, $O_2$, $H_2$), ultrasonics rapidly produce concentrated and much more stable emulsions. The droplets, after having settled down, do not coalesce, but form a grey sediment which does not entirely disappear even after many days. Since this effect is found, no matter whether hydrogen or oxygen is present, chemical action may be excluded. It is also improbable that the mercury particles act as gas electrodes of the nature of Frumkin's [2] particles of platinised charcoal, for it is known that mercury has no tendency to behave as a gas electrode. In any case, they cannot do so in nitrogen.

Feebly adsorbable electrolytes are of no account as to the resulting emulsions. More strongly adsorbable electrolytes cause the gas influence to become indistinct, while in the presence of true protective agents, such as soaps, gelatin or lysalbinic acid, the influence of the presence or absence of gas disappears entirely. We may recall the fact that, in the case of oil emulsions, the absence of gas cannot be compensated by the presence of protective agents.

[1] F. Rogowski and K. Söllner, *Z. physik. Chem.*, 1933, **166A**, 428.
[2] A. Frumkin and Donde, *Ber.*, 1927, **60**, 1816 ; N. Bach-Nikolajewna and A. Frumkin, *Koll. Z.*, 1928, **46**, 89.

These facts make it highly improbable that gases act with mercury emulsions in the same way as in oil emulsions.

It can be proved, moreover, that cavitation is of no importance whatsoever when emulsifying mercury :

(1) Emulsification takes place *in vacuo*, *i.e.*, under conditions where no effective collapse of cavities can occur, provided only that substances which favour stable emulsions are present (for instance protective agents, as just mentioned).

(2) Under high external pressure, whereas the water had only been saturated with gas at low pressure—thus producing conditions strongly disadvantageous to cavitation (see the preceding paper)—mercury was readily dispersed, so long as protective agents were present. These experiments were carried in the same way as described before, external pressures up to 8 atm. being applied.

Steam passed into the interface of mercury/water—a method most efficient for emulsifying oil/water systems owing to the collapse of cavities—had here no emulsifying effect.

Quite a different mechanism of emulsification had to be sought. W. T. Richards [3] already had assumed a mechanism, which we were able to confirm in all particulars. In a system of mercury and water, every mechanical operation easily leads to the formation of water bubbles under the surface of the mercury. It is not surprising that a similar process takes place when ultrasonic waves act upon the system. Richards was able to prove this to be true by showing that mercury, separated shortly after radiation, had a marked water content. He concluded, therefore, that the mechanism was " evidently closely parallel to the one described by Nordlund [4] who obtained similar emulsions by bubbling water through a mercury layer." On observing the mercury during radiation it can be seen that water bubbles, covered with a thin film of the metal, appear at the surface. When they burst a grey cloud of emulsion is driven into the water. We must evidently assume that the following series of processes takes place : Minute droplets of water are thrown into the mercury and unite in the interior ; the thin films of mercury separating them then burst and thus a drop of mercury emulsion is already formed in the interior of the metal. What happens at the surface is only the last step of this process. All efficient methods of dispersing mercury mechanically are based on the bursting of thin mercury films, as was already emphasised by Nordlund.

Before discussing the protective action of gases we will mention some experiments with organic liquids.

Substances such as pure petroleum-ether, benzene, toluene, xylene, ether, methyl alcohol, etc., give no emulsions or only extremely dilute ones ; nitrobenzene, higher alcohols, glycerin, etc., give somewhat concentrated emulsions. The mechanism turned out to be the same as when water was the dispersion medium, *i.e.*, a bursting of bubbles coated with a mercury film.

In the presence of protective agents such as rubber, marked emulsification always takes place, even in solvents such as petroleum-ether, which otherwise give no emulsion at all.

This shows that the difference between the different organic liquids is only due to differences in their stabilising properties : if the system is cooled down to a temperature near the melting-point of mercury, emul-

[3] W. T. Richards, *J. Amer. Chem. Soc.*, 1929, **51**, 1724.
[4] I. Nordlund, *Dissertation Uppsala*, 1918 ; *Koll. Z.*, 1920, **26**, 121.

sions are formed also in liquids, which coagulate at once at room temperature. This corresponds to Svedberg's [5] observations in organosols.

Both in water and in organic liquids the above-mentioned influence of gases was found. In liquids such as butyl alcohol, amyl alcohol, nitrobenzene, aniline, etc., the influence was especially marked. Although the emulsions show no obvious difference as to their concentration shortly after radiation, the stability in the gas-free systems is much less. After sedimentation the droplets quickly coalesce and unite with the bulk of the mercury, whereas in the gas-containing systems the sediment may easily be redispersed by merely shaking, and this even after a long time.

A stabilising action of gases must also be assumed with organic liquids. The influence of gases is, of course, less distinct in liquids where, owing to the small stability, the only emulsions obtained are too dilute. In liquids which give too stable emulsions, for instance very viscous liquids, the effect also cannot be observed.

The stabilising effect of gases is presumably general,[6] whereas the effects of gases mentioned in the preceding paper are characteristic for the action of ultrasonic waves.

A stabilising action of gases may appear somewhat enigmatical, but this assumption is not without precedent.

Cone, Tartar and Taylor [7] have found that Zsigmondy gold sols change their colour to a brighter red and have a higher precipitation value after being saturated with gas ; hydrogen and oxygen exert an influence in the same direction. But they did not observe any change in the velocity of cataphoretic migration after saturating with hydrogen.

It is known that the particles of aqueous sols adsorb marked amounts of gases ; this applies for both lyophobic and lyophilic sols. Thus, H. Garrett [8] has mentioned that the absorption coefficient for air is 50 per cent. higher in $3 \cdot 9$ per cent. aqueous $SiO_2$ sols than it is in pure water. Freundlich and Emslander [9] found a reversible adsorption of $CO_2$ on the colloids of beer. A. Findlay and co-workers [10] later investigated this phenomenon more thoroughly and found many cases of gas adsorption in colloidal solutions.

It is less generally known that these adsorbed gases may change the properties of the sols and other disperse systems. As was remarked by Garrett [8] the viscosity of $SiO_2$ sols is decreased by the adsorption of air. Spring [11] has found that the sedimentation volume of sand in water is augmented by the presence of gases.

The lowering of the surface tension of water and organic liquids by gases has been investigated in a wide range of pressures.[12]

[5] T. Svedberg, *Koll. Z.*, 1911, **9**, 153.

[6] It is intended to investigate this question in detail. Ultrasonics do not seem to offer a suitable method for this investigation. Oil/water and water/oil emulsions cannot be produced without gas being present, and with metal emulsions the de-gassing effect of ultrasonic waves may have an uncontrollable influence.

[7] W. M. H. Cone, H. V. Tartar, T. I. Taylor, *J. physic. Chem.*, 1932, **36**, 735.

[8] H. Garrett, *Dissertation Heidelberg*, 1903.

[9] F. Emslander and H. Freundlich, *Z. physik. Chem.*, 1904, **49**, 317.

[10] A. Findlay, *Koll. Z.*, 1908, **3**, 169 ; A. Findlay and Creighton, *J. Chem. Soc.*, 1910, **97**, 536 ; A. Findlay and collaborators, *ibid.*, 1912, **101**, 1459 ; 1913, **103**, 636 ; 1913, **103**, 1170 ; 1914, **105**, 291 ; 1914, **105**, 1297 ; 1915, **107**, 282 ; 1922, **121**, 1046.

[11] W. Spring, *Bull. Soc. Belg. Géol.*, 1903, **17** (part 2), Mém. 13.

[12] A. Kundt, *Ann. Physik (Wied.)* 1881, **12**, 538 ; K. Bönicke, *Dissertation Münster*, 1905 ; Th. W. Richards and E. K. Carver, *J. Am. Chem. Soc.*, 1921, **43**, 827. In H. Freundlich's *Kapillarchemie*, Vol. 1, p. 112, the pressure coefficient of the surface tension of water has been incorrectly calculated ; it must be 0·1 per cent. instead of 1 per cent. for Kundt's experiments.

We are as yet unable to visualise any plausible explanation for the protective action of gases which would hold both for water and for organic liquids ; it does not seem possible to correlate this effect in a simple manner with the change in ability to wet which is due to small amounts of foreign substances.

### Summary.

1. Mercury is emulsified by ultrasonic waves in the same way as by shaking. The mechanism consists in the bursting of bubbles of the second liquid coated with thin films of mercury.

2. Adsorbed gases stabilise mercury emulsions.

3. The concentration of the emulsions formed in different liquids depends upon the stabilising properties of the dispersion medium.

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# STUDIES ON SOL-GEL TRANSFORMATIONS. I. THE INVERSE SOL-GEL TRANSFORMATION OF METHYLCELLULOSE IN WATER.

By E. Heymann.

Reversible sol-gel transformations have often been discussed recently. The first investigations were carried out on the non-isothermal sol-gel transformation, especially of gels like gelatin and agar, where the transition from the sol state to the gel state occurs when the temperature is lowered.

In 1923 the reversible isothermal sol-gel transformation was first described by Szegvari and Schalek[1] in the case of inorganic gels like iron hydroxide and vanadium pentoxide, the transition from the gel to the sol being produced by mere shaking (thixotropy). Many of these transformations have been investigated by H. Freundlich and his co-workers,[2] especially in regard to the nature of the forces which keep the colloidal particles at a distance from each other, and the question whether there is any change of state of the water when the sol is transformed into the gel, *e.g.*, an increase of the orientation of water molecules. With regard to this last question, it seems to be established in the case of iron hydroxide and vanadium pentoxide sols, that there is no change of state of the water molecules when the sol is transformed into the gel.

There are, however, some curious examples of non-isothermal sol-gel transformations which have not yet been investigated thoroughly. For example, where the gel is formed at higher, and can be reversibly trans-

[1] Szegvari and Schaleck, *Kolloid-Z.*, **32**, 318 ; 1923, **33**, 326.
[2] H. Freundlich, *Kapillarchemie,*vol. II, 4th edition, page 615-632.

formed back into the sol, at lower temperatures.   The first good example was investigated by Szegvari[3] in the case of solutions of collodion in a mixture of amyl acetate and benzene.   Other examples found have been nitro-cotton in alcohol (J. M. McBain, C. E. Harvey and L. E. Smith[4]), the transition point being below room temperature, and solutions of sodium behenate in water (M. E. Laing[5]).   The last mentioned system has, however, not the same degree of reversibility as those first mentioned.

Excellent examples of such " inverse " sol-gel transformations, which are reversible and easily reproducible, are solutions of certain methyl celluloses in water, the investigation of which is dealt with in this paper.   Moreover, it will be shown that this system is interesting not only because the transformation is inverse but also because its investigation gives, especially if the results are compared with those obtained in the case of other sol-gel transformations, an interesting view-point as to the process of sol-gel transformation in general.

## I. Some Properties of Methylcellulose Solutions.

Special preparations of methylcelluloses with a certain content of the methoxyl group are soluble in water at low temperatures, but are pre-cipitated from these solutions when the temperature is raised (L. Lilien-feld[6]).   In some cases precipitation occurs as an opaque gel.   The experiments of the several investigators in regard to the solubility of the methylcelluloses do not agree.   Some have obtained water soluble products only with preparations of a medium methoxyl content, whereas others find that highly methylated preparations, corresponding to the trimethyl cellulose (45 per cent.), are also soluble in cold water.   The decisive factor in regard to the solubility, as well as to the form in which the precipitation or gel formation occurs, appears to depend largely on the origin of the cellulose as well as on the conditions under which the methylation is carried out ; that is to say, it depends on the degree of splitting of the cellulose " micelles " or " molecules " during the purifica-tion " of the cellulose and during the process of methylation.   Since it is not the purpose of this paper to go into the details of this question, only references to the literature will be given.[6]

The solubility of these compounds in water is attributed by Staud-inger and Schweitzer[7] to the formation of an oxonium hydroxide, in connection with the ether group, which becomes unstable at higher temperatures.   According to Staudinger the oxonium hydroxide is that part of the molecule which has affinity for water molecules and is thus responsible for the hydration.

For the following investigations methylcellulose of a methoxyl conten-of 35·4 per cent. was used.   It was a preparation of the I. G. Farbent industrie.[8]   This substance is almost completely soluble in cold water ; the very small proportion of insoluble matter was removed by centrifuging.

[3] Szegvari, *Koll. Z.*, 1923, **34**, 34.

[4] McBain, Harvey and Smith, *J. Physic. Chem.*, 1926, **30**, 347.

[5] Laing, *J. Chem. Soc.*, 1925, **127**, 275.

[6] Lilienfeld, *U.S. Pat.*, x, 1916, 1,188,376 ;   Denham and Woodhouse, *J. Chem. Soc.*, 1913, **103**, 1735 ;   1914, **105**, 2357 ;   Hirst, *J. Chem. Soc.*, 1923, **123**, 529 ; Karrer, *Helv. Chim. Acta*, 1924, **7**, 363 ;   Hess, *Ann. Chem.*, 1925, **442**, 461 ; 1926, **450**, 29 ;   Berl and Schupp, *Cellulosechemie*, 1929, **10**, 41.

[7] Staudinger and Schweitzer, *Ber.*, 1930, **63**, 2327.

[8] I have to thank Professor A. Schmidt (Frankfurt a/M) for kindly pro-viding me with a considerable quantity of this substance.

A 1·6 per cent. solution of this substance forms a somewhat viscous sol, which is transformed into an opaque gel between 40 and 50° C. Dilute solutions only flocculate after similar treatment. On cooling, the gel is readily re-transformed into the sol. This product contained about 0·5 per cent. of ash, consisting mainly of Ca, Fe and $SO_4$, which was partially removed by treating the technical product with hot water. The ash content after this treatment was about 0·2 per cent. (mainly $Fe(OH)_3$). The properties as described later are not changed appreciably by this treatment with hot water.

In some preliminary experiments the viscosity of these solutions and its change with temperature were investigated with an ordinary Ostwald viscometer (Fig. 1). The time of outflow $\tau$ decreases as expected, at first with incr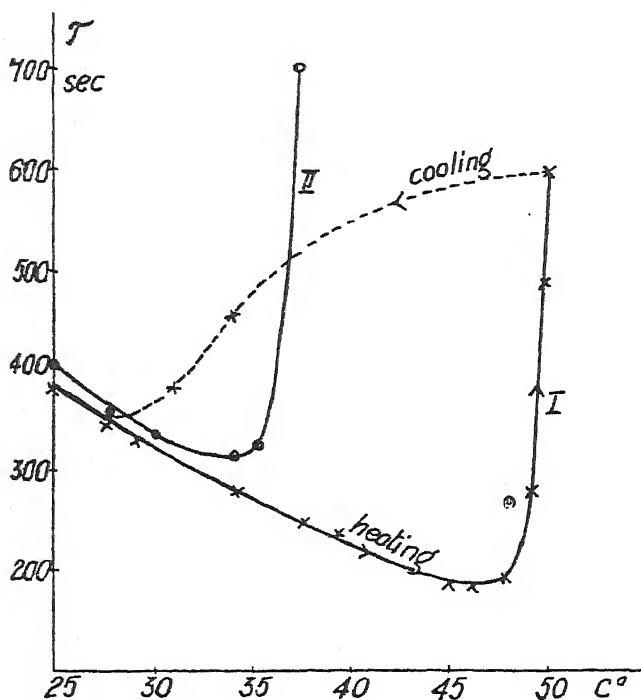easing temperature, but at certain temperatures, which are lower for higher concentrations and higher for lower ones, the direction of the curve changes, the viscosity increases very rapidly and the sol is transformed into a gel by a comparatively small further increase of temperature. If the solution is cooled, strongly pronounced hysteresis phenomena are observed. As Fig. 1 shows, the times of outflow at the same temperature are much higher — sometimes twice as high — when the solution is being cooled than when it is being heated.

FIG. 1.—I. Methylcellulose 1·56 per cent.
II. Methylcellulose 1·52 per cent. + 0·1 mol $K_2SO_4$.

If, however, the solution is cooled to room temperature the viscosity assumes its original value fairly quickly, showing that the sol-gel transformation is reversible (in regard to hysteresis phenomena in solutions which contain sulphate, see paragraph V.). At lower temperatures no change in viscosity can be observed when the solution is treated mechanically by shaking or by ultrasonic waves, whereas at higher temperatures, when the turning point of the curve is approached, thixotropic phenomena are found, the time of outflow after several suctions up and down being considerably lower than in the first measurement. The same effect can be produced by an application of ultrasonic waves. If, however, a somewhat stiff gel has once been formed it cannot be liquefied either by shaking or by ultrasonic waves.

If the gels are kept for a longer time at higher temperatures, syneresis

occurs. A 1·6 per cent. solution, for instance, which was kept at 80° for fifty days produced a considerable amount of water, about 20 per cent. of its own volume, the separated liquid being free from organic material. The amount of syneresis increases (as has already been observed by several authors with different systems) with decreasing concentration. If these systems are cooled, the viscosity shows a considerable decrease, sometimes about 50 per cent. The experiments of Berl and Schupp show that cellulose ether solutions are very stable systems, the methoxyl content not being changed by long treatment at higher temperatures. We have to assume, therefore, that the viscosity decrease after a long high-temperature treatment is due to a decrease in the polymerisation of the cellulose. But after a treatment of the solutions at 60° for a shorter time a decrease in viscosity occurs occasionally. This difficulty can be easily overcome if the solutions are kept for several days at about 70° C. ; after this treatment the sol-gel transformation proves to be reversible in regard to viscosity.

## II. Influence of Salts on the Sol-Gel Transformation.

If salts are added in comparatively small concentrations to solutions of methylcellulose the temperature of the sol-gel transformation is considerably changed. This influence has been investigated by measuring the " melting point " of the gels on cooling. It is true that the measurement of a " melting point " of a gel is somewhat inaccurate, since there is no sharp melting point, but merely a temperature interval in which the viscosity decreases so rapidly that the gel begins to flow. The influence is, however, so great that this method was quite sufficient to discriminate between the action of the several ions.

The melting interval was investigated in the following way : the sol was sealed in a test tube and heated to about 70° C. whilst it was transformed into the gel. Then the tube was hung horizontally in a beaker containing 1 litre of water at about 50° C., which was allowed to cool with continuous stirring, the temperature being observed, when the meniscus of the gel started to move. In Tables I. and II. the first number is the temperature when this occurred, whereas the second number corresponds to the temperature when the meniscus became horizontal. In this way comparable results were obtained since the cooling velocity was always approximately the same.

Tables I. and II. show the results which were obtained. In all cases the concentration of the gel was 1·6 per cent. and the concentration of the salt 0·2 molar.

| TABLE I. | | |
|---|---|---|
| | | *Melting point in °C.* |
| LiCl | . . | . 33·8–32·0 |
| NH$_4$Cl | . . | . 34·7–32·9 |
| NaCl | . . | . 34·0–32·0 |
| KCl | . . | . 34·0–32·0 |
| RbCl | . . | . 33·2–31·8 |
| CsCl | . . | . 33·2–31·3 |
| without salt | . | . 39·0–37·8 |

| TABLE II. | | |
|---|---|---|
| | | *Melting point in °C.* |
| K$_2$SO$_4$ | . . | . 25·0–23·0 |
| K-Tartrate | . | . 31·3–29·0 |
| K-acetate | . | . 34·5–33·0 |
| KCl | . . | . 34·5–32·5 |
| KBr | . | . 36·7–34·5 |
| KNO$_2$ | . . | . 38·1–35·5 |
| KNO$_3$ | . . | . 38·5–36·5 |
| KJ | . . | . 41·2–39·8 |
| KCNS | . | . 42·0–40·8 |

The cations have no marked influence. The anions, however, have a strong influence ; the sulphate ion lowers the melting interval to about 25°, the sulphocyanate raises it to about 42°. The influence of the sulphate is also to be seen in the viscosity curve II. in Fig. 1. In this experiment the K$_2$SO$_4$-concentration was only 0·1 molar, and therefore the temperature of

the beginning of gel formation was higher than the corresponding tempera-
ture in the melting point measurement.   Moreover the temperatures corres-
ponding to the beginning of the viscosity increase do not coincide with the
melting points because of the syneresis.

The well-known lyotropic series proved to be valid, the order being
CNS, I, $NO_3$, $NO_2$, Br, Cl, acetate, tartrate, $SO_4$.

The CNS and I ions have, in this system as well as in many others,
liquefying properties.

Addition of organic solvents usually increases the melting-point, if
they are added in considerable proportions.   The sols no longer form a
gel when alcohol or acetone are added in considerable quantities (30 per
cent.).   If, however, the action of the homologous alcohols be compared,
no marked difference between the several alcohols can be found.

The same lyotropic series is found, when the precipitation of methyl-
celluloses is investigated.   Table III.
shows the minimum concentrations
of salts which are necessary for floccu-
lation.   In these experiments the
ammonium salts were used instead of
the potassium salts, because of their
greater solubility.   The sulphate ion
has the strongest flocculating pro-
perties, as it precipitates methy-
cellulose solutions in comparatively
small concentrations, whereas the
corresponding concentrations of iodide
and sulphocyanate are much higher.

TABLE III.—Concentration of
Methylcellulose : 1·8   per
Cent.

| | Flocculation concentration of salt in mol. per litre. |
|---|---|
| $(NH_4)_2SO_4$ | 0·40 |
| $NH_4$-acetate | 0·66 |
| $NH_4Cl$ | 3·0 |
| KI | 3·6 |
| $NH_4CNS$ | > 4·3 |

Thus the influence of salts in small concentrations on the sol-gel
transformation and in high concentrations on the precipitation are quite
parallel.   This suggests that the causes of both processes are the same.
As it has often been assumed that the precipitation of hydrophilic
colloids by salts is due to a dehydration of the particles, it seems very
likely that the sol-gel transformation in the system methylcellulose-
water is also caused by dehydration.   The investigation of every physical
property which will be dealt with in the following paragraphs confirms
this assumption.

One general remark may be made at this point : The expression
methylcellulose " particles " is used purposely, because no assumption
will be made as to whether the solutions contain single thread-shaped
macromolecules or micelles.   It is, however, likely that diluted solutions
contain mainly single molecules, whereas the more concentrated ones
may also contain micelles (H. Mark).

## III. Viscosity and its Anomalies.

The viscosity was measured by Ubbelohde viscometers, which
allow the viscosity to be measured at various pressures, that is to say at
variable rate of shear, the pressure during one measurement remaining
sufficiently constant if the manostat is large enough.

For these experiments a manostat of 10 litres was used, the pressure
being observed with a
mercury manometer for
the higher pressures and
a water one for the lower
pressures.   The dimen-
sions of the two visco-
meters were :

| | A. | B. |
|---|---|---|
| Volume of the bulb | 14·63 c.c. | 14·82 c.c. |
| Length of the capillary | 14·5 cm. | 14·0 cm. |
| Radius of the capillary | 0·58 mm. | 0·36 mm. |

The viscometers were calibrated with a 40·0 per cent. sugar solution, the viscosity of which is 0·05187 g. cm.$^{-1}$ sec.$^{-1}$ at 25·0° C. and 0·03249 g. cm.$^{-1}$, sec.$^{-1}$ at 40° C. When sugar solutions were measured the product of the time of outflow and the pressure was constant, indicating that the sugar solutions obeyed Poiseuille's law and the measurements were carried out within the range of laminar flow.

In Poiseuille's formula for the laminar flow

$$\eta = \frac{\pi r^4 . p . t}{8 . l . v},$$

where $r$ is the radius of the capillary, $t$ the time of outflow of a volume $v$ under the pressure $p$, and $l$ the length of the capillary. $r$, $l$, and $v$ are constant, if the same viscometer is used, and consequently the product $p \cdot t$, which is proportional to $\eta$, is constant. The anomalies, which very often occur in colloidal solutions are characterised by the fact, that $p \cdot t$ decreases with increasing rate of shear. If in any liquid the rate of shear is increased over certain values (Reynolds number), the flow becomes turbulent, and in this case the product $p . t$ increases with increasing rate of shear. In the present experiments the streaming velocities were such that no turbulent flow occurred.

Fig. 2 shows the results obtained with methylcellulose solutions in water. If Poiseuille's law is rigidly obeyed, $\eta$ should be independant of pressure and the curves should be parallel to the pressure axis. However, at lower



FIG. 2.—Methylcellulose 1·72 per cent.

temperatures the deviations from Poiseuille's law are not great in solutions of 1·5 — 1·8 per cent. In less concentrated solutions, for instance a 1 per cent. solution, the deviation becomes very small indeed. Addition of salts (Fig. 3) changes the absolute value of the viscosity ; thus both KCNS and $K_2SO_4$ lower it in 0·1 molar solution. But the inclination of the $\eta$-$p$-curves, which is an estimate of the degree of anomaly, is practically the same as in the solutions with pure water. If water, as solvent, is replaced by mixtures of water and alcohol or water and acetone (Fig. 4), considerable increases as well as decreases in viscosity occur, according to the composition of the mixture ; but in these cases,
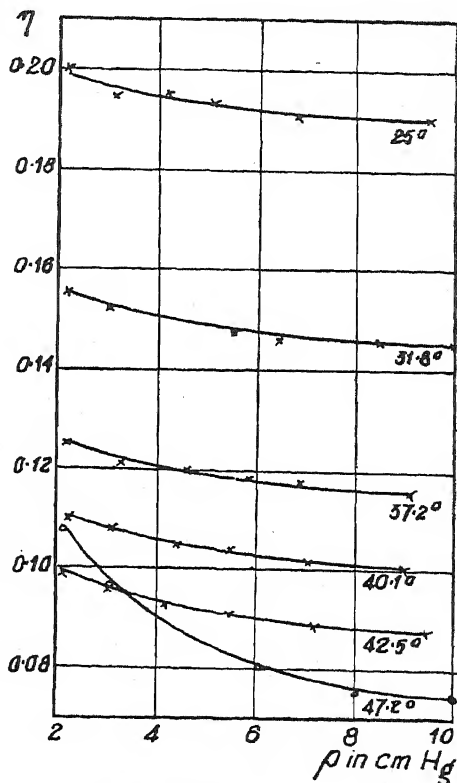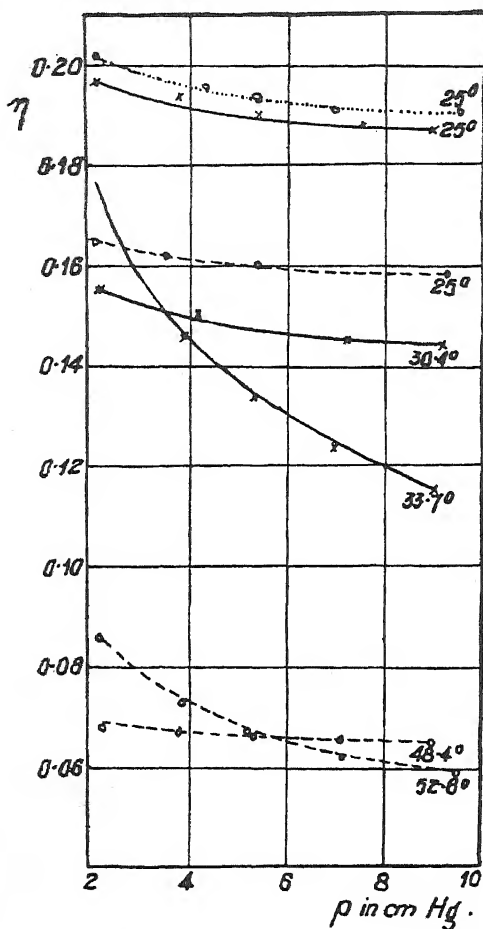
too, the inclination of the $\eta$-$p$-curves does not change considerably, as compared with sols in pure water.

If, however, the temperature at which the sol-gel transformation sets in is approached, the inclination of the curves becomes greater and typical curves of anomalous viscosity are obtained. The viscosity coefficient $\eta$, calculated according to Poiseuille's law, is very much dependent on the rate of shear. Moreover, in this temperature region the viscosity is decreased by mechanical treatment, such as sucking the liquid up and down in the capillary several times. The effect of mechanical treatment becomes still more evident in the action of ultrasonic waves. It is very likely that these anomalies at higher temperatures are due to a gel structure, which is being built up when the sol is being transformed into a gel and which is more and more destroyed when the shearing forces are increased.

The much smaller anomalies at lower temperatures, however, are due to a different cause. It is certainly not a "structure" in the sense in which this expression was used above, which is responsible for the anomaly in the viscosity. Although the viscosity is somewhat higher at lower pressures than at higher ones, it is not changed by mechanical treatment, and even ultrasonic waves do not change it. That



FIG. 3.—Methylcellulose 1·72 per cent.

····· Without addition of salt.
—— Addition of 0·1 mol. $K_2SO_4$.
---- Addition of 0·1 mol. $KCNS$.

is to say, at lower temperatures, the conditions, which are responsible for the anomaly, are restored immediately after mechanical treatment. It is possible that the anomaly is due to the fact that the thread-shaped molecules hinder each other in their movement. But the possibility that the thread-shaped molecules tend to an orientation parallel to the direction of the flow with increasing streaming velocity might also be

taken into consideration (H. Mark,[10] W. Kuhn [11]) ; it must be remembered in this connection that the sols of ethylcellulose show streaming double refraction at comparatively small streaming velocities (Signer [12]).

During the last few years the anomalies of viscosity in colloidal solutions have often been discussed (Bingham,[13] Buckingham,[14] Weissenberg, Eisenschitz, Rabinowitsch [15]). It is likely that no general answer can be given and that the explanation will depend on the type of system. At present it seems to be premature to discuss these results in detail on the basis of such papers, before direct measurements of elasticity in the system methylcellulose-water have been carried out, either by Schwedow's [16] or Hatschek's [17] method or by a method determining the damping of an oscillating disc, recently developed by E. G. Richardson [18] as well as by Eisenschitz and Philippoff.[19]

## IV. Changes in Viscosity at Constant Temperature during the Sol-Gel Transformation.

The viscosities of more dilute solutions only show

Fig. 4.

25° Methylcellulose 1·55 per cent. in :
I. Water.
II. 25 alcohol + 75 water.
III. 75 alcohol + 25 water.
IV. 50 acetone + 50 water.
V. 84 glycerin + 16 water.
[volume per cent.]

[9] Bingham and Jackson, *Scient. Paper Bureau of Standards*, 1917, Nr. 298.
[10] H. Mark, *Physik und Chemie der Cellulose*, Berlin, 1932, p. 78.
[11] W. Kuhn, *Koll. Z.*, 1933, **62**, 269.
[12] R. Signer, *Z. physik. Chemie*, 1930, **150A**, 265.
[13] E. C. Bingham, *Fluidity and Plasticity*, New York, 1922.
[14] Buckingham, *Proc. Amer. Test. Mat.*, 1921, **21**, 1154.
[15] Eisenschitz, B. Rabinowitsch and Weissenberg, *Mitt. Deutsch Material-prüfungsamt, Sonderheft*, 1929, **9**, 91 ; Eisenschitz and B. Rabinowitsch, *Ber.*, 1932, **64**, 2522 ; Weissenberg, *Abh. Preuss. Akad. Wissensch. Phys. Math. Kl.* Nr. **2**.    [16] Schwedoff, *J. Physique*, 1889, **8**, 341.
[17] Hatschek and Jane, *Koll. Z.*, 1926, **39**, 300.
[18] E. G. Richardson, *Trans. Farad. Soc.*, 1933, **29**, 494.
[19] Eisenschitz and Philippoff, *Naturw.* 1933, **21**, 529.

very small deviation from Poiseuille's law (Fig. 5) and therefore, these solutions may be used to investigate the temperature coefficient of viscosity. In Fig. 6 the relative viscosity $\eta_r = \eta_s/\eta_w$, where $\eta_s$ is the viscosity coefficient of the sol and $\eta_w$ the viscosity of the water, is plotted against temperature. At first $\eta_r$ falls steadily with rise in temperature,
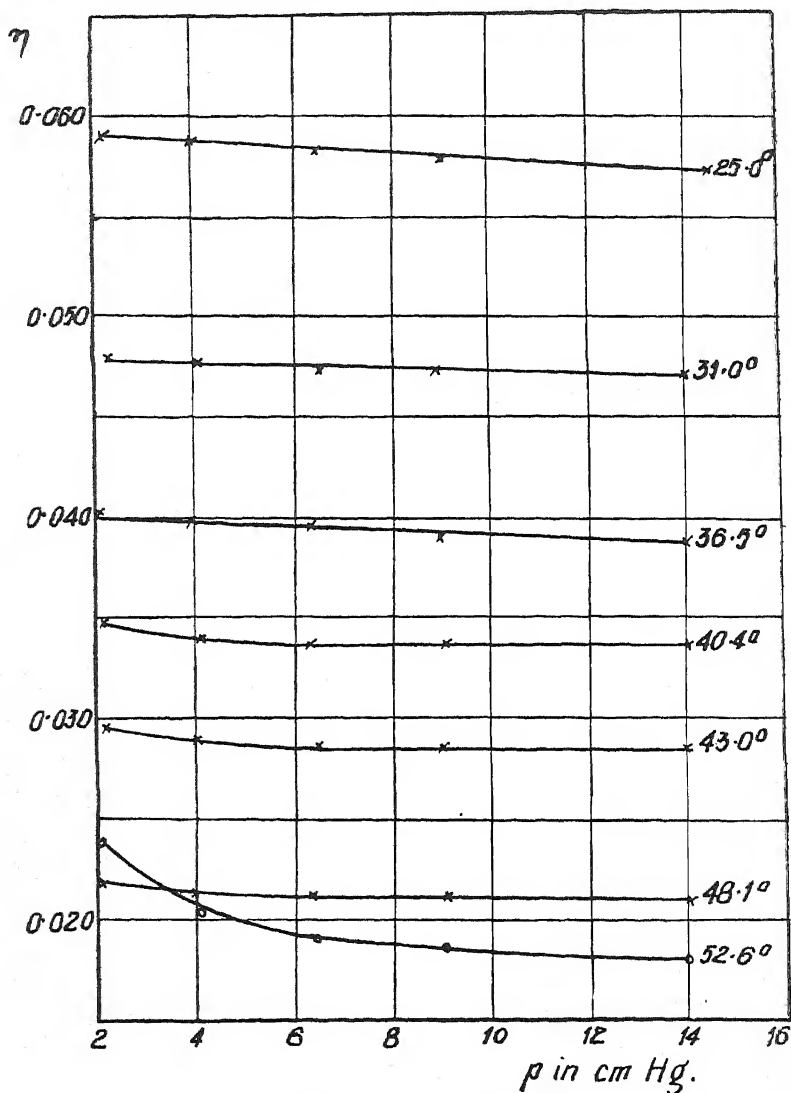


FIG. 5.—Methylcellulose 0·965 per cent.

but at point A, about 10 degrees below the point of beginning transformation (point B), the viscosity curve falls more steeply, the temperature coefficient of viscosity thus becoming greater.[24] At higher temperatures, of course, the usual increase due to the gel formation sets in.

The first part of the curve, showing the steady decrease of the re-

lative viscosity, is a common feature of many solutions of hydrophilic compounds, such as sugar. This means simply that the temperature
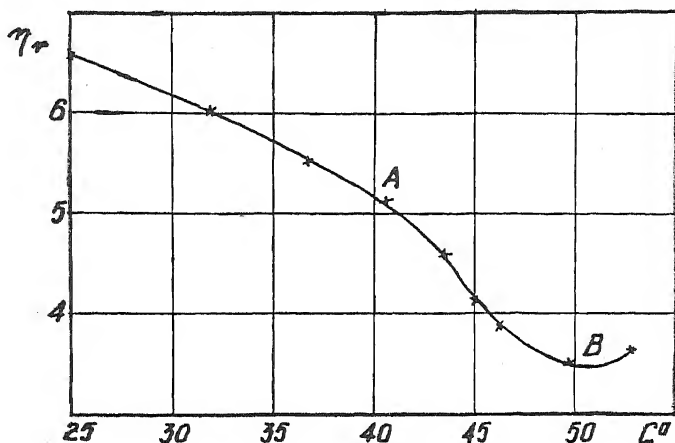


FIG. 6.—Methylcellulose 0·965 per cent.

coefficient of the solution is greater than that of the solvent, a fact which has to be attributed to a decrease of hydration with rise in temperature (Hatschek,[20] Porter,[21] Fickentscher and Mark,[22] Haller[23]), the effective volume of the dissolved particle, that is to say, particle plus hydration layer, thus becoming smaller.[24] The fact that in this system the negative temperature coefficient of the relative viscosity becomes even greater in a certain temperature interval below
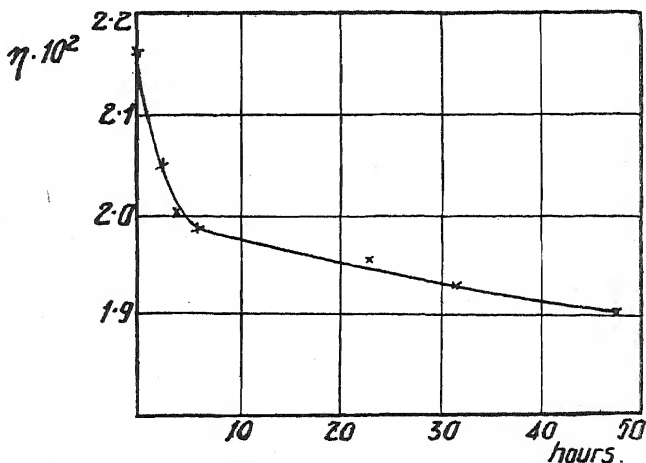


FIG. 7.—44·1°.

[20] Hatschek, *The viscosity of liquids*, London, 1928.
[21] Porter, *Trans. Farad. Soc.*, 1917, **13**, 1.
[22] Fickentscher and Mark, *Koll. Z.*, 1925, **49**, 135.
[23] W. Haller, *Koll. Z.*, 1931, **56**, 257.
[24] Staudinger and Schweitzer have found a similar behaviour in aqueous solutions of methylcellulose which did not form a gel at higher temperature, but only a turbid sol. In their experiments the temperature coefficient of the relative viscosity increases suddenly when the sol becomes opalescent.

the transformation temperature can be interpreted by the assumption that dehydration occurs before the sol is transformed into the gel.[25]

If the velocity of such a process is slow, at certain temperatures, it should be possible to observe a reversible decrease in viscosity at constant temperature, before it increases because of the gelation. A process such as this was observed.

Fig. 7 and Table IV. show the change of viscosity of a 0·995 per cent.

TABLE IV.

| Time in Hours. | Viscometer II. | | | 44·1° C. |
|---|---|---|---|---|
| | $p$ in cm. Hg. | $t$ in sec. | $\eta$. | |
| 0 | 4·10 | 115·5 | 0·0217 | solution |
| | 6·52 | 72·2 | 0·0216 | clear |
| | 9·15 | 51·3 | 0·0216 | |
| 2 | 4·06 | 109·2 | 0·0203 | |
| | 6·37 | 70·2 | 0·0205 | slightly opalescent |
| | 9·11 | 49·0 | 0·0205 | |
| $3\frac{1}{2}$ | 4·17 | 105·4 | 0·0201 | |
| | 6·30 | 69·6 | 0·0201 | |
| | 9·26 | 47·4 | 0·0201 | |
| $5\frac{1}{2}$ | 4·06 | 106·8 | 0·0199 | |
| | 6·56 | 66·2 | 0·0199 | increasing opalescence |
| | 9·15 | 47·7 | 0·0199 | |
| 24 | 4·21 | 102·2 | 0·0197 | |
| | 6·36 | 67·4 | 0·0196 | |
| | 9·21 | 46·3 | 0·0195 | |
| 31 | 4·42 | 95·2 | 0·0193 | |
| | 6·35 | 66·0 | 0·0192 | |
| | 9·14 | 45·8 | 0·0192 | |
| 47 | 6·45 | 64·3 | 0·0190 | turbid |
| | 9·15 | 45·4 | 0·0190 | |

The solution was then put into ice water for half an hour and measured again at 44·1°.

| | | | | |
|---|---|---|---|---|
| | 4·38 | 108·1 | 0·0217 | solution |
| | 6·45 | 73·4 | 0·0217 | clear |

solution when it is aged at 44·1°. The viscosity drops from 0·0216, at first quickly, then more slowly, to 0·0190 in 47 hours ; there are practically no deviations from Poiseuille's law during this period. This process is completely reversible. If, after ageing, the solution is cooled in ice water and then replaced in the thermostat at 44·1°, the original value of the viscosity is again obtained, and the process can be repeated a number of times. The decrease in viscosity is accompanied by an increase of the intensity of the Tyndall light. Therefore, the possibility of its being due to a depolymerisation of the methylcellulose, which, moreover would not be reversible, is definitely excluded. We have, therefore, to assume that

[25] It is unlikely that the decrease of the relative viscosity with rise in temperature is caused by a splitting of " micelles " because, as some preliminary experiments with the " Stufenphotometer " of Zeiss show, the intensity of the Tyndall light increases considerably with rise in temperature.

this reversible drop in viscosity at constant temperature is due to the de-hydration of the particles, a process which, in our system, is the first step of the sol-gel transformation.

This becomes even more evident if the system is aged at temperatures which are one or two degrees higher. At $45\cdot0°$ the viscosity at first decreases, but after two hours reaches a minimum value, after which it increases continuously, owing to the progressive transformation into the gel. Furthermore, it is significant that at this temperature, already after a very short time, Poise-uille's law is no longer obeyed and the apparent viscosity is higher at lower pressures than at higher ones, indicating that the gel forma-tion sets in very soon (Fig. 8). At $46\cdot1°$ this process is even more evi-dent. At still higher tem-peratures, for instance at $47\cdot4°$, the velo-city is so great that the first drop in viscos-ity cannot be observed.

Bungen-berg de Jong [26] in his investi-gations on the sol-gel trans-formation of agar, has at-tempted to find a similar decrease in viscosity as the first step of the trans-
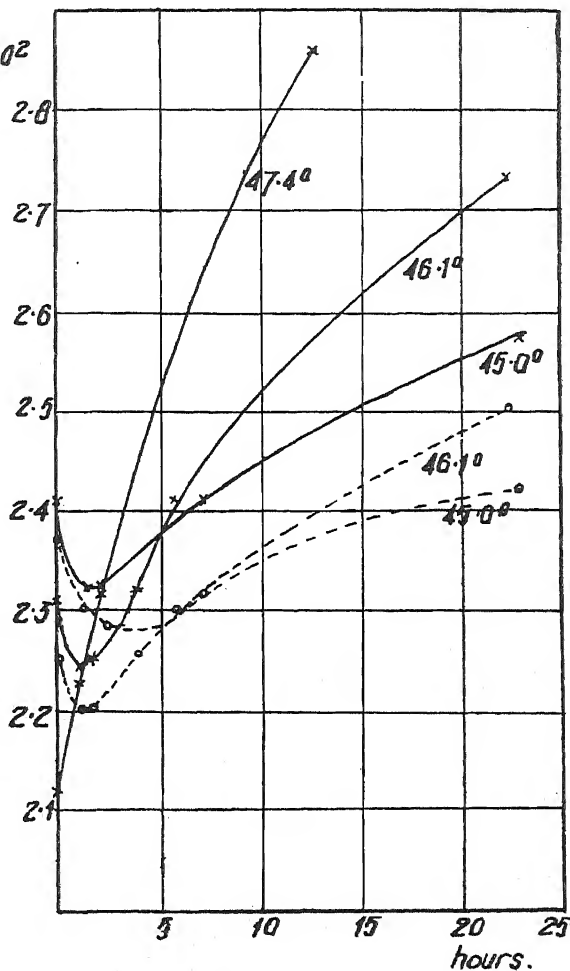


FIG 8.

—— p = 2 cm. Hg.          - - - - p = 4 cm. Hg.

formation. Such a process, however, is absent in the case of agar, and Bungenberg de Jong therefore assumed that in this system the formation of the gel is not caused and not accompanied by a decrease in hydration. This assumption is no doubt true. It even seems that in the case of agar the sol-gel transformation is accompanied by an increase in hydration of the particles, since Krishnamurti [27] has found, that the volume decreases

[26] Bungenberg de Jong, *Rec. Trav. Chim. Pays-Bas*, 1928, **47**, 797.
[27] Krishnamurti, *Current Science*, 1934, II, 351.

during the transformation of an agar sol into a gel, indicating that the orientation of the water molecules round the particle is likely to increase.

## V. A Hysteresis Phenomenon.

If the variation of viscosity of a 1·62 per cent. solution (containing 0·1 mol. of potassium sulphate) with pressure is measured at 25°, curve I. is obtained (Fig. 9), indicating only a comparatively small anomaly in the viscosity. If the solution is now heated for four days to about 45°, until completely gelified, brought back to 25°, where it is liquefied, and the viscosity measured, curve II. is obtained. It is not surprising that the viscosity becomes very abnormal after the treatment at 40°, because, as the transformation temperature of systems containing sulphate is rather low, the gel is not completely retransformed into the sol at 25°.



It is surprising, however, that after this treatment the viscosity at higher pressures is lower than the original viscosity. This phenomenon seemed to be difficult to explain. When the solution was afterwards cooled in ice water for half an hour and measured again at 25°, curve IV. was obtained practically coinciding with curve I.

An explanation was found, however, by introducing treatment with ultrasonic waves. The apparatus has been described by H. Freundlich, F. Rogowsky and K. Soellner.[28] A piezo-electric quartz was excited by an alternating current at 20,000 volts; the frequency being about 250,000 per second. In this case the energy applied to the system was of the order of magnitude of about 50 watt.

FIG. 9.

If the solution after treatment at 45°, yielding the viscosity curve II., is treated with ultrasonic waves and measured at 25°, curve III. is obtained. The striking anomaly of viscosity is removed, but the viscosity is more than 10 per cent. smaller than originally. If the solution is now cooled in ice water and measured again at 25°, curve IV. is obtained, the viscosity having practically attained the original value.

It is now clear what has happened. At 45° the sol is transformed into a gel with dehydrated particles (paragraph IV). If the system is

[28] Freundlich, Rogowsky and Soellner, *Koll. Beih.*, 1933, **37**, 223.

brought down to 25°, the breaking down of the gel structure as well as the rehydration of the particles does not occur completely in a short time, as indicated by curve II. : the viscosity varies considerably with pressure ; at high pressures, whilst the gel structure is destroyed, the viscosity is smaller than the original one.   But if the system is treated with ultrasonic waves, the gel structure is completely destroyed, whereas the particles are still dehydrated, as is shown by curve III., which is considerably below curve I.[29]   Only after treatment in ice water are the particles rehydrated completely and the original viscosity restored (curve IV. coinciding with curve I.).

## VI. Volume Change during the Sol-Gel Transformation.

If the sol-gel transformation is accompanied by a decrease in hydration of the collodial particles, a change in volume may be expected.   This volume change will probably be positive, since there is much evidence that the layer of water molecules round a colloidal particle under the influence of its attractive forces has a higher density, that is to say a smaller specific volume than the free water. An increase in volume during the sol-gel transformation was found. For the experiments a sensitive dilatometer (Fig. 10) and an electric thermostat, constant within 0·003° were used.   The full details will be given in a later paper.

The sol was contained in I., the mercury in II.   The tap $a$ allowed the height of the meniscus of the mercury in the capillary ($b$) to be varied.   Leakage of the tap $c$ was avoided by coating with picein which proved to be very satisfactory.   The tap was of 2 mm. bore, through which the sol was run in using a very fine funnel.   The bulb ($d$) is a trap to prevent any sol which might get into part II. of the dilatometer thus passing into the capillary.

The capillary had a radius of 0·23 mm.   Thus a change of meniscus in the capillary of 1 cm. corresponded to a volume change of 0·0016 c.c. The volume of part I., which contained the sol, was approximately 80 c.c. ; this varied slightly in different experiments according to the volume of the mercury used.



*Dilatometer.*

*Capillary.*

*b*

*a*

*c*

*sol.*     *II.*

*I.*     *d*

*Mercury.*

FIG. 10.

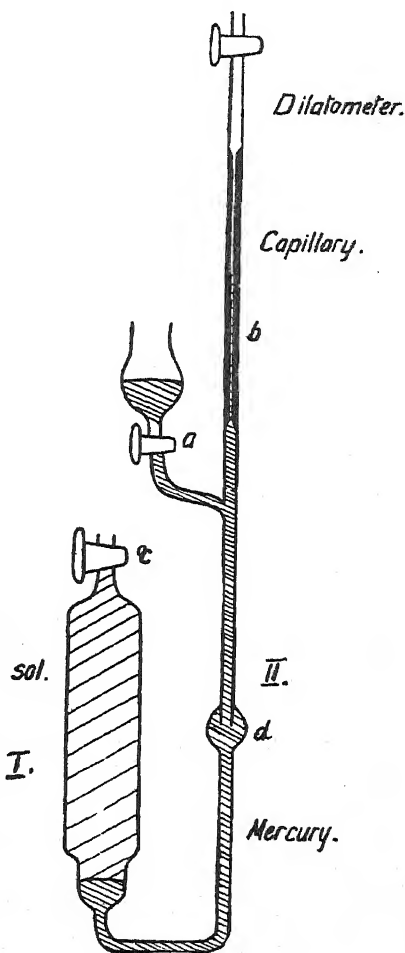[29] A similar effect can be produced by sucking the solution through the capillary at high pressures.

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In Table V. an example of one measurement is given. The volume of the sol was 83 c.c. Its concentration was 1·62 per cent., and it contained 0·1 molar $K_2SO_4$, the latter being added in order to lower the temperature of the sol-gel transformation for experimental convenience. The dilatometer containing the sol was placed in the thermostat at 35·7°, the temperature remaining constant within 0·003°. The first reading was taken one hour after placing the dilatometer in the thermostat.

TABLE V.

| Time in Hours. | Reading of the Meniscus. | Temperature (Relative) on Beckmann Thermometer. |
|---|---|---|
| 1 | 13·21 | 5·140 |
| 3 | 13·36 | 5·142 |
| 26 | 13·60 | 5·143 |
| 50 | 13·82 | 5·142 |
| 122 | 13·84 | 5·144 |
| 150 | 13·83 | 5·143 |

During this experiment the sol was transformed into a very loose gel. The change in position of the meniscus corresponded to a change in volume of 0·00096 c.c. Thus the volume of the sol increased by 0·0012 per cent. Actually the volume change was somewhat larger, since the change during the first hour was not taken into account, blank experiments showing that the sol did not assume the temperature of the thermostat until this period had elapsed. Extrapolation to zero time is not, however, justified owing to unavoidable experimental errors.

After the experiment, the dilatometer was placed in ice water, where the gel was retransformed into the sol, then transferred back into the thermostat. After one hour the reading was 13·23 ; which was practically the original value. The process was thus shown to be completely reversible.

In another experiment the volume of the sol was measured at 35·7° the sol transformed into a gel by heating in a bath of 55° and the volume measured again 35·7°. It was found that in this case the volume change is higher, namely about 0·0016 per cent. The reason for the higher value in this case is that the sol is transformed into a much stiffer gel than in the first mentioned one.

The full details of these and other experiments, as well as a criticism of the accuracy, will be communicated in a later paper.

## VII. Solvation and Immobilisation ; the Mechanism of Dehydration in the System Methylcellulose-Water.

It has already been pointed out by several authors (Wo. Ostwald, W. Haller [30]), that the solvation of a colloidal particle or a molecule of high molecular weight must not of necessity be due to an adsorption of the molecules of the solvent by the attractive forces between the latter and the colloidal particle (" adsorption-solvation "). There may also exist a kind of solvation due to the shape of the particle. This may happen if the particle is long or has a complicated structure. Thus many molecules of the solvent can be influenced by the particle in such a way, that they cannot be regarded as free (" Immobilization "), although there may be no attractional forces between these solvent molecules and the particle. Staudinger [31] goes still further and is inclined to regard this as the main process (see also the calculations of Eisenschitz [32] and of W. Kuhn [33]).

[30] Wo. Ostwald, *Koll. Z.*, 1926, **46**, 259 ; W. Haller, *Koll. Z.*, 1929, **49**, 47 ; 1931, **56**, 257.
[31] H. Staudinger, *Koll. Z.*, 1930, **51**, 71.
[32] Eisenschitz, *Z. physik. Chem.*, 1931, **158A**, 78.
[33] W. Kuhn, *Koll. Z.*, 1934, **68**, 2.

There is, however, one experimental test, which will show definitely whether there is an adsorption solvation of the particles or not. The phenomena of decrease in volume of the system, which occurs when the solid matter is dissolved in the liquid or when it is swelling in the liquid, and the volume change, when the sol is transformed into the gel, can only be understood if there is an adsorption-solvation of the particles. The solvent layer due to the attractive forces between the particles and the solvent molecules is, however, supposed to have a higher density than the free liquid ; the immobilized solvent having most probably the same density as the free solvent.
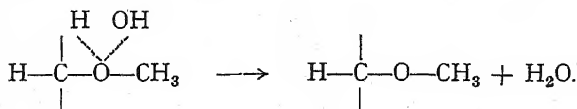
A second test, which was mentioned by Haller, is the negative temperature coefficient of the relative viscosity, since the adsorption of solvent molecules is likely to decrease with rise in temperature, with the result, that the effective volume of the particle becomes smaller. It is, however, doubtful, whether this test is as reliable as the first, especially if the rise in temperature is accompanied by a splitting or by a partial coagulation of the particles.

Gelatin (Svedberg [34]) as well as agar (Krishnamurti) show a change in volume during swelling or during the sol-gel transformation respectively. It is, therefore, certain, that in these cases, there is solvation due to the attractive forces between the particles and the molecules of the solvent.

In the system methylcellulose-water adsorption-solvation is also certainly prevalent. This is clearly indicated by the fact that the volume increases, whilst the sol is transformed into the gel. Moreover the relative viscosity has a negative temperature coefficient.

It is, however, likely, that in all these cases there is also an additional solvation, which is due to the occurrence of immobilization, as the particles of all these compounds mentioned above are certainly not spherical.

One fact, however, requires further explanation. The curves of the decrease in viscosity at constant temperature, as well as the corresponding measurements of the volume increase during the sol-gel transformation of the methylcellulose sols, show that the dehydration of the particles is a somewhat slow process. This fact would be difficult to explain if we had to assume that the dehydration merely consisted of a process, in which the forces between the particles and the water molecules are removed, the water of the hydration layer being transformed into free water ; the volume of the particles thus becoming smaller, with the result that the viscosity decreases. To explain the slow dehydration velocity a more complicated mechanism must be considered. One possible mechanism may be suggested : the primary process is the decomposition of the methylcellulose oxonium hydroxide which, according to Staudinger and Schweitzer, is present in the solutions at low temperatures and which becomes unstable when the temperature is raised.

$$\begin{array}{c} \text{H} \quad \text{OH} \\ | \diagdown \diagup \\ \text{H—C—O—CH}_3 \end{array} \longrightarrow \begin{array}{c} | \\ \text{H—C—O—CH}_3 + \text{H}_2\text{O}. \\ | \end{array}$$

This process, in which one water molecule, which was bound by secondary valencies, is separated from each ether group, is most probably not

[34] The Svedberg, *J. Amer. Chem. Soc.*, 1924, **46,** 2673.

the whole process of dehydration, since it has to be assumed that the oxonium-hydroxide is hydrated, whereas the insoluble methyl ether of the cellulose does not attract water molecules at higher temperatures. This decomposition of the methylcellulose oxonium hydroxide, accompanied by the dehydration of the particle can be a slow process, since we know, from the experiments of C. S. Hudson [35] in the case of the dehydration of lactose, that these processes of chemical dehydration can proceed very slowly. As a second stage in the process the dehydrated methylcellulose molecules associate with one another, probably with the formation of micelles with parallel oriented chain-molecules, this being in accord with many other observations on the behaviour of cellulose compounds. By this process new water molecules, which have however, been immobilized by the long shaped chain molecules are drawn away from them. This assumption of a mechanism of dehydration combined with an oriented coagulation gives a possible explanation for the fact that the volume change and the viscosity decrease occur simultaneously with an increase of the intensity of the Tyndall light.

### VIII. Several Types of Sol-Gel Transformations.

It is possible to draw some conclusions from the experiments described in this paper in regard to the mechanism of several types of sol-gel transformations, or more especially in regard to the changes of state of the dispersion medium that occur during the gelation. This picture may still be a rough one and it may be necessary to vary it to some extent when more experimental data are obtained. Nevertheless, the existing data are sufficient to give a discrimination between three types of sol-gel transformations.

To the first class belong the sol-gel transformations of several inorganic sols, such as iron hydroxide and vanadium pentoxide, yielding in many cases thixotropic gels. In these cases there is most probably no change of state of the water molecules during the transformation. The dielectric constant, when measured in a wave length region where the colloidal particles contribute nothing to the orientation polarisation does not change during the transformation (Kistler [36]), indicating that fixation or orientation of water molecules does not occur to any appreciable extent during this process. This is, moreover, supported by the fact that the volume does not change during the gel formation ; dilatometric experiments on the gel formation of a thixotropic iron hydroxide sol will be communicated in a later paper.

To the second class belong agar and probably gelatin. Here the already strongly hydrated particles of the sol become even more hydrated when the gel is formed. This is clearly indicated by the fact that the volume decreases while the gel is formed (Krishnamurti). Moreover the fact, found by Bungenberg de Jong, that the viscosity, measured at constant temperature, increases at once and that no decrease in viscosity can be found, supports this assumption.

To the third class belongs the sol-gel transformation of methylcellulose in water, the investigation of which is described in this paper. In the sol the particles are hydrated. The hydration is decreased, before gel formation takes place. This is indicated by the positive volume change and by the fact that, at constant temperature, the

[35] C. S. Hudson, *Z. physik. Chem.*, 1904, **50**, 373.
[36] Kistler, *J. Physical Chem.*, 1931, **35**, 815.

viscosity decreases at first, simultaneously with an increase of the intensity of the Tyndall light, and shows the usual increase due to gel formation only after a period. It is very likely that in this class the dehydration of the particles is the first step of the sol-gel transformation. While this process proceeds coagulation occurs to a certain degree, and the particles so formed build up a loose network, that is to say the gel. The gels of this group are not as stable as the gels of the second group, but show a strong tendency towards syneresis and in some cases, after ageing during a longer period, towards crystallisation in the macroscopic sense of this word.

To this type belong probably all those sol-gel transformations where the gel is formed by a process whereby the dissolved compound becomes insoluble, either by a change in temperature, or when one liquid is replaced by another one, or on the other hand, when the gel is formed by a chemical reaction yielding an insoluble substance. Many of those gels are not reversible and many of them are somewhat unstable. Solutions of viscose forming a gel with a tendency towards syneresis belong to this group, since, when those solutions are aged, the viscosity decreases at first and then increases (Mark [37]).

## Summary.

The formation of gels by aqueous solutions of methylcellulose on heating and reversal to sols on cooling, has been investigated.

(1) Addition of salts in small concentrations changes the temperature of the transformation, the lyotropic series in regard to the anions being valid, e.g., sulphocyanate rising, sulphate lowering the transformation temperature. In high concentrations addition of salts produces precipitation, the lyotropic series of the anions being valid in this case also.

(2) The viscosity and its anomalies have been measured. The anomalies are small at low temperatures, but increase considerably, when the transformation temperature is approached. In this region viscosity shows thixotropic effects, whereas at low temperatures no such effects are found. It is likely that the small anomalies at low temperatures are due to causes different from those operating at higher temperatures, where the anomalies are certainly due to the formation of a gel structure.

(3) At temperatures, where the sol-gel transformation proceeds slowly, the viscosity, measured at constant temperature, at first decreases and only shows the usual increase after some time.

(4) The volume increases during the transformation.

(5) Both the volume increase as well as the initial viscosity decrease indicate that the gel formation is due to a dehydration of the particles. The mechanism of the formation of a methylcellulose gel is discussed.

(6) The two possible kinds of hydration (adsorption-hydration and immobilisation) are discussed ; the volume change during the transformation, in particular, suggests that in this system adsorption-solvation prevails.

(7) Some hysteresis phenomena of the viscosity of solutions, aged at higher temperatures, can readily be explained by the assumption that the gel contains dehydrated particles.

(8) The several types of sol-gel transformations are discussed. To the first class belong those, where no change in state of the solvent occurs (many hydrophobic inorganic systems). In the second class the gel formation is accompanied by an increase in hydration of the particles (e.g., agar). In the third class the gel formation is the consequence of a

[37] H. Mark, *Physik und Chemie der Cellulose*, Berlin, 1932, p. 260.

dehydration of the particles (e.g., methylcellulose and many other gels with tendency towards syneresis).

I am greatly indebted to Professor F. G. Donnan, F.R.S., for the generous hospitality which he has given me in his laboratory as well as for his constant interest in the work. Furthermore, I am very much indebted to Professor H. Freundlich for much valuable advice and helpful criticism.

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            *London, W.C. 1.*

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# THE TITRATION CURVES OF PROTEIN FIBRES.

By Dorothy Jordan Lloyd and P. Betty Bidder.

Some recent studies on the swelling of protein fibres (Jordan Lloyd and others, 1933 and 1934) suggested that the number and nature of the collateral binding forces holding the long parallel molecules together in the fibre have a greater influence in controlling swelling in aqueous solutions than the number of charged centres capable of entering into salt linkages with any acid or alkali present. At the time, however, no titration curves of protein fibres were available in the literature and therefore the determinations recorded below were made. Since then the titration curve for wool has been recorded by Speakman and Stott (1934). This curve is similar in form to the curve for horse hair given below and shows certain characteristics found in all the fibre titration curves. These will be discussed later.

## Experimental Methods and Results.

Three types of protein fibres were taken : (1) purified collagen fibres prepared from oxhide as previously described (Jordan Lloyd, Marriott and Pleass, 1933) ; (2) silk fibroin fibres prepared from surgical sutures. These as obtained had an ash content of 0·45 per cent., but after extracting with $N/100$ hydrochloric acid and washing until free from acid this fell to 0·02 per cent ; (3) purified horse hair also prepared from surgical sutures. As obtained, the ash content was about 1 per cent., but after extracting with $N/100$ hydrochloric acid and washing till acid free, this fell to 0·15 per cent ; (4) besides these, a titration curve was made of iso-electric gelatin (ash content 0·02 per cent.) in the solid state.

The method of determining the combining power of the fibres for acid and alkali was as follows : 0·100 g. of fibre was placed in a test tube with 10 ml. of standard acid or alkali or proportionate quantities, say 0·500 to 50 ml. The tubes were corked and those containing alkali were waxed over. Contact between fibre and solution was maintained for two days, a time which preliminary experiments showed to be sufficient for equilibrium to be attained. 5 ml. were then pipetted off from each tube into a clean dry test tube, a suitable indicator was added and all alkaline solutions were sealed off from the air with about half an inch of heavy paraffin. The $p_H$ of the dilute solutions were then determined by titrating 10 ml.

of Messrs. British Drug Houses " Universal Buffer " with standard acid or alkali to obtain a colour match with the corresponding indicator. This method, which is due to Cameron (1929), is the best available when dealing with small quantities of unbuffered dilute alkalies (or even acids) since it involves minimum handling of the solutions and consequently minimal error due to absorption of the carbon dioxide of the atmosphere or to adsorption of hydrogen or hydroxyl ions on glass surfaces. With the more concentrated solutions, determination were made by direct titrations with standard reagents from a micro-burette.

The titration curves obtained in this way are shown in Fig. 1 together with an electrometric titration curve of the gelatin obtained in the more orthodox manner with a glass electrode from a 1 per cent. solution. The experimental figures for this curve are due to Miss W. B. Pleass (1931).
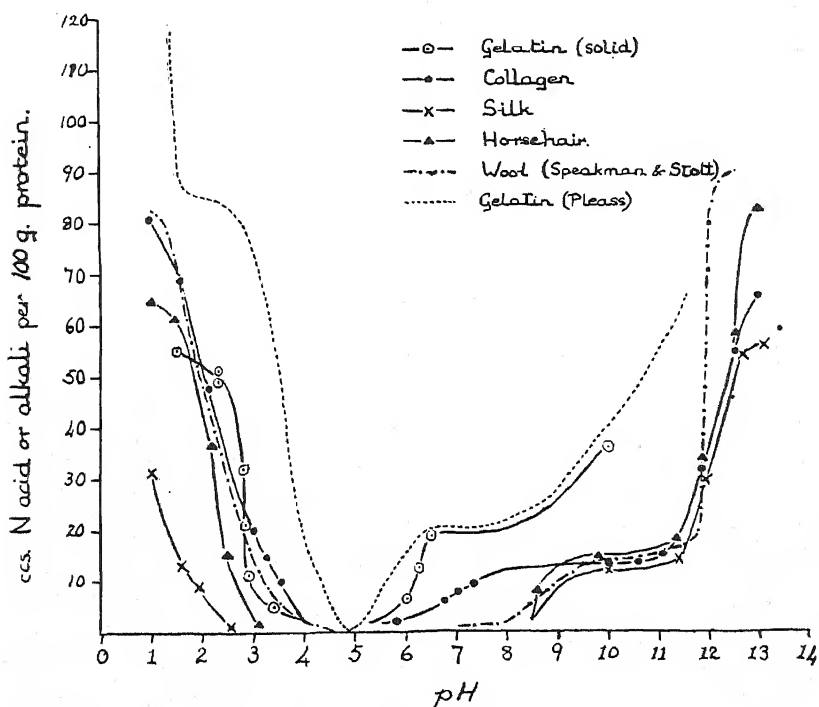


FIG. 1.

The alkaline curve has not previously been recorded. It is obvious that out of the proteins examined, combination occurs with acid or alkali on either side of a sharply defined iso-electric point only where the protein is dispersed throughout the system as a sol or gel. Even with the swollen gelatin forming a separate phase, there is an indication, more marked on the acid side, of a widening of the iso-electric point into an iso-electric " zone." With the protein fibres this becomes very marked.

In order to define the limits of the iso-electric zones of the different proteins, a series of buffer solutions was made up using the " Universal Buffer " of Messrs. British Drug Houses. 25 ml. of the standard strength of the " Universal Buffer " were adjusted and brought to a volume of 50 ml. Into these solutions the different proteins were introduced in the proportion of 0·1 g. of dry protein to 10 ml. of buffer solution. A suitable indicator was added to each tube and the following day the tubes were

TABLE I.

| Initial $p_H$. | Indicator. | Silk. | Hair. | Colla-gen. | Gelatin. Solid. | Gelatin. ∥ Gel. ∅ |
|---|---|---|---|---|---|---|
| 2·0 | $p.$ methyl red | ? | ? | .. | .. | .. |
| 2·5 | {benzyl-aniline-azo-benzene sulphonic acid} | O | O | + + | + + | .. |
| 3·0 | ,, ,, ,, | O | O | + + | + + | .. |
| 3·5 | ,, ,, ,, | O | O | (+) | + | + + |
| 4·0 | {"Universal" indicator (British Drug Houses)} | O | O | O | (+) | + + |
| 4·5 | ,, ,, ,, | O | O | O | O | + |
| 5·0 | ,, ,, ,, | O | O | O | O | O |
| 5·5 | ,, ,, ,, | O | O | O | — | — — |
| 6·0 | ,, ,, ,, | O | O | (—) | — | .. |
| 6·5 | ,, ,, ,, | O | O | (—) | — — | .. |
| 7·0 | ,, ,, ,, | O | O | — | — — | .. |
| 7·5 | ,, ,, ,, | O | O | .. | .. | .. |
| 8·0 | ,, ,, ,, | O | O | .. | .. | .. |
| 8·5 | ,, ,, ,, | (—) | O | .. | .. | .. |
| 9·0 | ,, ,, ,, | — | — | .. | .. | .. |

(+ + signifies considerable rise ; + definite rise ; (+) slight rise ; O no visible change ; (—) slight fall, etc. ; .. indicates no experiment.)

compared for colour tint with a control set containing no protein. The results are given in Tables I and II, + indicating that a rise, — that a fall of $p_H$ value had occurred in the presence of the protein. A zero sign (O), indicating no visible change, must be interpreted as meaning that the change in $p_H$ (if any) is certainly less than 0·1 in value, say 0·05 for most eyes. At the concentration of buffer used this means that less than 0·04 ml. of $N/10$ acid or alkali has been absorbed by 0·1 g. protein from 10 ml. of buffer, $i.e.$ equivalent to less than 4 ml. of $N$ acid or alkali per 100 g. protein.

TABLE II.

| Initial $p_H$. | Indicator. | Gelatin (Solid). | Gelatin (gel.). |
|---|---|---|---|
| 4·0 | Bromo-cresol Green | + | + + |
| 4·2 | ,, ,, ,, | + | + + |
| 4·4 | ,, ,, ,, | (+) | + + |
| 4·6 | ,, ,, ,, | O | + |
| 4·8 | ,, ,, ,, | O | (+) |
| 5·0 | ,, ,, ,, | O | O |
| 5·2 | "Universal" Indicator | — | O |
| 5·4 | ,, ,, | — | — |
| 5·6 | ,, ,, | — | — |

## Discussion.

The titration curve shown for gelatin is a measure of the acid or base combined with the protein. In the case of the solid gelatin and the protein fibres, it is strictly speaking only a measure of the acid or base which has passed from the outer solution into the solid gelatin or fibre. Not all of this will be combined with the protein. The error, however, in interpreting the titration curve as a curve of combined acid or base will be very slight in the case of the horse-hair and silk fibres, since these show very little swelling. The error will be greater with the collagen which swells more and greatest with the solid gelatin which swells considerably. Since the error will always be in the direction of increasing the values of the

ordinates, it does not invalidate the points dealt with below in considering the interpretations to be put on the curves.

Two points arise fairly clearly from the titration curves given in Fig. 1. The first is that the titration curves show a general, though not complete, similarity to the swelling curves of the proteins in acid and alkali ; the second is that the form of the titration curve could not have been predicted simply from a knowledge of the amino-acid constitution of the protein in question. Salt formation between proteins and acids or bases occurs by the formation of an electro-valent link between an ion of the electrolyte and a charged centre on a side chain or, less frequently, a terminal group of the protein molecule.

The most recent analyses available Dakin, 1920; Abderhalden and Wells, 1905; Vickery and Block, 1930 and 1931) show the following composition of the fibrous proteins in di-basic or di-carboxylic residues :—

|        |            | Gelatin (and Collagen). | Horse Hair. | Wool (Sheep). | Silk-Fibroin. |
|--------|------------|-------------------------|-------------|---------------|---------------|
| Bases. | Lysine     | 5·9                     | 1·1         | 2·3           | 0·25          |
|        | Arginine . | 8·2                     | 7·6         | 7·8           | 0·74          |
|        | Histidine  | 0·9                     | 0·6         | 0·66          | 0·07          |
| Acids. | Glutaminic | 5·8                     | 3·7         | —             | 0·0           |
|        | Aspartic . | 3·4                     | 0·3         | —             | —             |

Silk is practically free from carboxylic side chains and keratin contains a fair number. In spite of this the titration curves in alkaline solution run a very similar course. The sudden uptake of base at about $p_H$ 11·5 is common to all the fibrous proteins and is accompanied by considerable swelling, and, as shown by microscopical evidence, a considerable loosening of the structure. Again, though in acid solution silk fibroin, as might be expected, absorbs considerably less acid than collagen or keratin, the sudden increase in acid fixation which takes place at about $p_H$ 3 is common to all the fibres and is accompanied by swelling and a disruption of the structure.

Speakman and Stott have pointed out that where salt linkages between amino and carboxylic groups of the side chains of proteins are present, that combination with strong acids and strong bases will only occur outside the limits of the $p_H$ range 5-7 (using the appropriate ionisation constants for the respective amino acids as the basis of the calculation). Our curves suggest that linkages of this type are present not only in natural fibres but also even to some extent in dried gelatin.

In addition to these salt linkages between different protein molecules, a comparison of the titration curves for gelatin and collagen, which are chemically closely similar, and a further comparison of the curves for keratin and silk fibroin, which are chemically somewhat different, suggests that structural cross-linkages between the peptide chains of the protein molecules of a nature different from the ordinary salt linkages also exist in the fibres, and exert considerable influence on the availability of the charged centres of the protein molecules for electrolytic reactions with the small ions of the ordinary strong acids and alkalies.

## Summary.

A study of the fibrous proteins shows that, with increasing compactness of fibre structure, there is an increasing extension of an iso-electric zone within which combination with acid or alkali does not occur or only occurs to a very limited extent.

At $p_H$ values < 3 or > 11·5, there is a sudden increase in the amount

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of acid or alkali combining with the protein that is not determined by the amino-acid constitution of the protein. The increase in absorbed electrolyte is accompanied by a disruption of the fibre structure.

Even between the iso-electric point (or zone) of the protein and the $p_H$ values of 3 and 11·5 respectively, the titration curves are influenced not only by amino-acid constitution but also by the structure of the fibres. This is especially apparent in the $p_H$ range of 3-9.

### BIBLIOGRAPHY.

Abderhalden and Wells, *J. physiol. Chem.*, 1905, **46**, 31.
Cameron, *J.A.L.C.A.*, 1929, **24**, 76.
Dakin, *J. Biol. Chem.*, 1920, **49**, 499.
Jordan Lloyd, Marriott and Pleass, *Trans. Farad. Soc.*, 1933, **29**, 554.
Jordan Lloyd and Marriott, *Trans. Farad. Soc.*, 1933, **29**, 1228 ; 1934, **30**, 944.
Pleass, *Biochem.J.*, 1931, **25**, 1943.
Speakman and Stott, *Trans. Farad. Soc.*, 1934, **30**, 539.
Vicery and Block, *J. Biol. Chem.*, 1930, **86**, 107 ; 1931, **93**, 105.

# KINETICS OF THE REACTION BETWEEN POTASSIUM THIOCYANATE AND IODINE IN AQUEOUS SOLUTION.

## By R. O. Griffith and A. McKeown.

In solutions which are not too acid, $CNS^-$ reacts with $I_2$ according to

$$CNS^- + 4I_2 + 4H_2O \rightarrow SO_4^{--} + 7I^- + 8H^+ + CNI \quad . \quad (1)$$
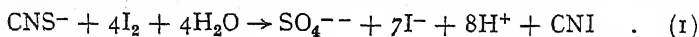
In acid solution owing to displacement of the equilibrium

$$CNI + I^- \rightleftharpoons CN^- + I_2$$
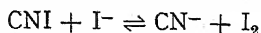
over to the right-hand side, the *net* reaction is

$$CNS^- + 3I_2 + 4H_2O \rightarrow SO_4^{--} + 6I^- + CN^- + 8H^+ \quad . \quad (2)$$
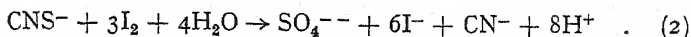
Hitherto the kinetics of the reaction have been studied only by Angelescu and Popescu,[1] who carried out experiments in presence of $NaHCO_3$ or of $Na_2HPO_4$. They inferred that the rate-determining step in the process is a reaction between $CNS^-$ and $IO^-$, but apart from the theoretical treatment of their results being clearly unsound, their data are insufficient to establish a mechanism. We have therefore undertaken a fresh study of the reaction under a fairly wide range of experimental conditions. The outcome has been to show that the reaction is a very complex one, whose detailed mechanism we have so far not been able to elucidate. It presents, however, a number of points of interest, and the results obtained together with certain general conclusions are now communicated.

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[1] Angelescu and Popescu, *Z. physik. Chem.*, 1931, **156A**, 258 ; *Bull. Soc. Chim. Rômania*, 1932, **14**, 25.

## Experimental.

Kinetic experiments have been carried out at temperatures between 20° and 40° under a variety of conditions. They include experiments (1) in buffered solutions (phosphate, phthalate, acetate, and oxalate) and (2) in unbuffered solutions (*i.e.*, of high acidity). The chemicals used were of A. R. standard. Various preparations of KCNS and other thiocyanates were used (for some of which our thanks are due to Mr. V. J. Occleshaw) ; all gave identical results. Reaction mixtures were contained in glass-stoppered flasks, blackened to exclude light and maintained in thermostats kept constant to ± 0·03°. Samples taken from time to time were run into acid and their iodine content estimated by titration with thiosulphate. In all our experiments, even those with highest [H⁺] and lowest [I⁻], it may be shown by applying Kovach's data [2] for the equilibrium

$$CNI + H^+ + I^- \rightleftharpoons HCN + I_2$$
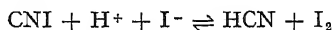
that, at least up to 80 per cent. conversion of the $I_2$ by reaction with CNS⁻, the *net* reaction measured was (1). Since, however, the titration of the iodine was effected in acid solution, it was necessary, in order to obtain the concentration of iodine during the experiment, to multiply the differences from the initial titre by 4/3 and subtract these from the initial titre.

For the majority of our experiments in buffered solutions it was found that to a first approximation the dependence of the rate of reaction on [$\Sigma I_2$], [$\Sigma KCNS$] and [I⁻] is given by

$$- \frac{d[\Sigma I_2]}{dt} = k' \frac{[\Sigma I_2][\Sigma KCNS]}{[I^-]^2} \qquad . \qquad . \qquad . \qquad (3)$$

where [$\Sigma I_2$] is concentration of titratable iodine,

$$[\Sigma KCNS] = [\Sigma KCNS]_{init.} - \tfrac{1}{4}\{[\Sigma I_2]_{init.} - [\Sigma I_2]\},$$

and [I⁻] is concentration of iodide ion, allowance having been made for formation of $I_3^-$. As will be shown, this kinetic equation is only approximately correct, but for purposes of comparison values of $k'$ calculated as indicated have been used for all experiments with buffered solutions. Throughout, velocity constants have been evaluated with concentrations in moles per litre and time in minutes.

### Experiments in Buffered Solutions.

Preliminary experiments in phosphate and acetate buffers showed that, except under conditions to be mentioned later, the reaction is unimolecular with respect to $\Sigma I_2$. In the majority of our experiments [$\Sigma I_2$]$_{init.}$ was 0·0033 or 0·0012. The order with respect to $\Sigma KCNS$ may be inferred from the data of Table I.

TABLE I.—$t = 20°$.

| Phosphate Buffers. [KI] = 0·175. | | | | Acetate Buffers. [NaAc] = 0·2 ; [HAc] = 0·2. | | | |
|---|---|---|---|---|---|---|---|
| [Na₂HPO₄]. | [KH₂PO₄]. | [ΣKCNS]. | $k'$. | [KI] = 0·025. | | | |
| 0·1 | 0·1 | 0·00486 | 0·0195 | [ΣKCNS] | 0·00486 | 0·00972 | 0·0394 |
| 0·1 | 0·1 | 0·0197 | 0·0201 | $k'$ | 0·00101 | 0·00114 | 0·00194 |
| 0·2 | 0·2 | 0·00486 | 0·0347 | [KI] = 0·05 | | | |
| 0·2 | 0·2 | 0·0197 | 0·0364 | | | | |
| 0·04 | 0·2 | 0·00486 | 0·00594 | [ΣKCNS] | 0·00486 | 0·0394 | 0·0788 |
| 0·04 | 0·2 | 0·0197 | 0·00702 | $k'$ | 0·00095 | 0·00146 | 0·00196 |

[2] Kovach, *Z. physik. Chem.*, 1912, **80**, 107.

It will be seen that in all cases the constants increase with increasing [$\Sigma$KCNS]. In phosphate buffers, however, the increase is small, except in the acid range of the buffer, *i.e.*, when the ratio [KH$_2$PO$_4$]/[Na$_2$HPO$_4$] is large. With acetate buffers, the increase in $k'$ with increasing [$\Sigma$KCNS] is fairly marked ; further, with high concentrations of KCNS the values of $k'$ fall slightly with time in each experiment, an indication probably that the rate of reaction is ceasing to be strictly proportional to $\Sigma$I$_2$.

The effect of iodide on the velocity has been studied under a variety of conditions. Typical examples are given in Table II.

TABLE II.—$t = 20°$.

| Acetate Buffers. [NaAc] = 0·2 ; [HAc] = 0·2. [$\Sigma$KCNS] = 0·00486. | | | | Phosphate Buffers. [Na$_2$HPO$_4$] = 0·2 ; [KH$_2$PO$_4$] = 0·2. [$\Sigma$KCNS] = 0·00471. | | | |
|---|---|---|---|---|---|---|---|
| [KI] | 0·0125 | 0·025 | 0·05 | [KI] | 0·0875 | 0·1312 | 0·175 |
| $k'$ | 0·00108 | 0·00101 | 0·00095 | $k'$ | 0·0408 | 0·0376 | 0·0347 |

Here, and indeed under all conditions we have studied, the values of $k'$ decrease with increasing [I$^-$]. This means that the order with respect to iodide ion is somewhat more negative than $-2$ ; in phosphate buffers, for example, under the conditions of Table II, the order is about $-2\cdot2$. Since the rate in general is strictly proportional neither to [$\Sigma$KCNS] nor to $1/[I^-]$,[2] comparisons in the data which follow have so far as is possible been made between experiments in which both [$\Sigma$KCNS] and [KI] were maintained constant.

To determine the effect of [H$^+$] on the reaction velocity, experiments have been carried out in oxalate and phthalate buffers, in addition to those in acetate and phosphate buffers. Considering first the results obtained in phosphate buffers these are summarised in Table III. and Fig. 1.

TABLE III.—$t = 20°$ ; [$\Sigma$KCNS] = 0·00471 ; [KI] = 0·175.

| [Na$_2$HPO$_4$]. | $\frac{[Na_2HPO_4]}{[KH_2PO_4]}$ =5. | 4. | 2. | 1. | $\frac{1}{2}$. | $\frac{1}{4}$. | $\frac{1}{8}$. | $\frac{1}{11}$. | $\frac{1}{16}$. |
|---|---|---|---|---|---|---|---|---|---|
| 0·2 | — | 0·0683 | 0·0455 | 0·0347 | 0·0259 | 0·0188 | 0·0159* | — | — |
| 0·1 | 0·0438 | — | 0·0250 | 0·0198 | 0·0155 | 0·0128 | 0·00908 | 0·00799 | — |
| 0·02 | 0·0256 | — | 0·0122 | 0·00754 | 0·00539 | 0·00430 | — | — | 0·00305 |

$$* \ \frac{[Na_2HPO_4]}{[KH_2PO_4]} = \frac{2}{11}.$$

In Fig. 1 the values of $k'$ in the three series are plotted against [Na$_2$HPO$_4$]/[KH$_2$PO$_4$], that is, against a quantity proportional to $1/[H^+]$. It is seen that for each series the plot is a straight line on the alkaline side, but on the acid side a fall in $k'$ occurs, the fall being the more pronounced

the larger the concentration of $[KH_2PO_4]$. The linear portions of these plots are well reproduced by the equations :

Series with 0·2 $M$ $Na_2HPO_4$: $k' =$
$$0·0235 + 0·0111 \ [Na_2HPO_4]/[KH_2PO_4].$$
Series with 0·1 $M$ $Na_2HPO_4$: $k' =$
$$0·0128 + 0·0062 \ [Na_2HPO_4]/[KH_2PO_4].$$
Series with 0·02 $M$ $Na_2HPO_4$: $k' =$
$$0·00324 + 0·00444 \ [Na_2HPO_4]/[KH_2PO_4].$$

In acetate buffers, on the alkaline side of $pK_a$ a similar linear relationship obtains. Experiments were carried out with solutions containing
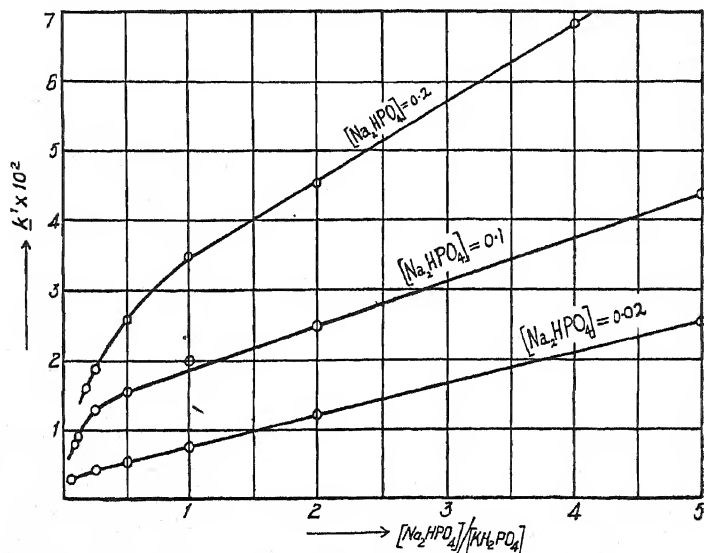


FIG. 1.

initially NaAc and either none or a low concentration of HAc. The concentration of acetic acid thus increases during the experiment, while the ratio [NaAc]/[HAc] and the velocity constants $k'$ fall. Similar experiments were conducted with mixtures of $K_2C_2O_4$ and $KHC_2O_4$. Table IV. gives the results of one series of experiments with acetate buffers, while Table V. summarises the whole of these data.

TABLE IV.—$t = 20°$ ; $[\Sigma KCNS] = 0·00471$ ; $[KI] = 0·025$ ; $[NaAc] = 0·20$.

| [NaAc]/[HAc] | 108 | 75·6 | 58·9 | 47·6 | 40·8 | 21·5 | 17·2 | 10·75 | 9·46 | 4·67 | 1 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $k'$ . $10^3$ (obs.) | 4·05 | 3·40 | 2·84 | 2·59 | 2·38 | 1·72 | 1·59 | 1·44 | 1·35 | 1·17 | 1·02 |
| $k'$ . $10^3$ (calc.) | 4·42 | 3·40 | 2·87 | 2·51 | 2·30 | 1·64 | 1·55 | 1·35 | 1·31 | 1·16 | 1·03 |

$$k' \ (calc.) = 1·01 \ . \ 10^{-3} + 3·15 \ . \ 10^{-5} \ \frac{[NaAc]}{[HAc]}.$$

It is to be noted that the values of $k'$ of Table V. hold only for ratios of [NaAc] to [HAc] greater than 1 ; on the acid side of $pK_a$ the velocity constants exhibit the same type of behaviour as that obtaining in phosphate buffers, $i.e.$, they fall progressively further from the linear relationships of Table V. as the acidity is increased.

TABLE V.—$t = 20°$.

| [ΣKCNS]. | [KI]. | [NaAc]. | $k'$. |
|---|---|---|---|
| 0·00471 | 0·025 | 0·20 | $1·01 \ . \ 10^{-3} + 3·15 \ . \ 10^{-5}[NaAc]/[HAc]$ |
| 0·00486 | 0·025 | 0·08 | $0·463 \ . \ 10^{-3} + 2·76 \ . \ 10^{-5}[NaAc]/[HAc]$ |
| 0·00486 | 0·05 | 0·08 | $0·440 \ . \ 10^{-3} + 2·60 \ . \ 10^{-5}[NaAc]/[HAc]$ |
| 0·01943 | 0·05 | 0·20 | $1·21 \ \ . \ 10^{-3} + 3·36 \ . \ 10^{-5}[NaAc]/[HAc]$ |
| 0·01943 | 0·05 | 0·08 | $0·564 \ . \ 10^{-3} + 2·41 \ . \ 10^{-5}[NaAc]/[HAc]$ |
| 0·01884 | 0·05 | 0·20 [$K_2C_2O_4$] | $4·53 \ \ . \ 10^{-4} + 4·38 \ . \ 10^{-6}[K_2C_2O_4]/[KHC_2O_4]$ |

Finally, a few experiments in phthalate buffers have been carried out. They show that the velocity exhibits the same type of dependence on [ΣKCNS] and [KI] as that in other buffers, but the effect of a wide variation of [$H^+$] has not been tested.

TABLE VI.—$t = 20°$.

| [ΣKCNS]. | [KI]. | [NaK Phthalate]. | [KH Phthalate]. | $k'$. |
|---|---|---|---|---|
| 0·00471 | 0·025 | 0·09629 | 0·1037 | 0·00109 |
| 0·00486 | 0·025 | 0·09629 | 0·02592 | 0·00117 |
| 0·00471 | 0·05 | 0·09629 | 0·1037 | 0·000965 |
| 0·00471 | 0·05 | 0·1605 | 0·03952 | 0·00167 |
| 0·01884 | 0·05 | 0·1605 | 0·03952 | 0·00203 |

The data of Tables III.-V. suggest that the reaction is one catalysed by bases, that is proton-acceptors in terms of Lowry's and Brønsted's definition, including therefore the anions of weak acids in addition to $OH^-$ ions. The velocity constant in a buffer solution would then be expressible in terms of an equation of the type :

$$k' = k_S \ [Salt] + k_{OH^-} [OH^-] = k_S \ [Salt] + k_{OH^-} \frac{K_W \ [Salt]}{K_A \ [Acid]}.$$

where $k_S$ and $k_{OH^-}$ are the specific velocity constants of the reaction catalysed respectively by anions of the weak acid and by $OH^-$, $K_W$ is the ionic product of water and $K_A$ is the ionisation constant of the weak acid of the buffer. The values of $k_S$ and $k_{OH^-}$ obtained from these data are given in Table VII. Those of $k_{OH^-}$ are based on a value of $K_W$ of $10^{-14}$, and the following values of $K_A$ : phosphoric (2nd) $8·8 \times 10^{-8}$, acetic $1·8 \times 10^{-5}$, and oxalic (2nd) $7·1 \times 10^{-5}$.

TABLE VII.—$t = 20°$.

| Buffer. | | | [ΣKCNS]. | [KI]. | [Salt]. | $k_S$. | $k_{OH^-}$. |
|---|---|---|---|---|---|---|---|
| Phosphate | . | . | 0·00471 | 0·175 | 0·2 | 0·118 | $9·8 \ . \ 10^4$ |
| ,, | . | . | 0·00471 | 0·175 | 0·1 | 0·128 | $5·5 \ . \ 10^4$ |
| ,, | . | . | 0·00471 | 0·175 | 0·02 | 0·162 | $3·9 \ . \ 10^4$ |
| Acetate | . | . | 0·00471 | 0·025 | 0·2 | $5·05 \ . \ 10^{-3}$ | $5·7 \ . \ 10^4$ |
| ,, | . | . | 0·00486 | 0·025 | 0·08 | $5·8 \ \ . \ 10^{-3}$ | $5·0 \ . \ 10^4$ |
| ,, | . | . | 0·00486 | 0·025 | 0·08 | $5·5 \ \ . \ 10^{-3}$ | $4·7 \ . \ 10^4$ |
| ,, | . | . | 0·01943 | 0·05 | 0·2 | $6·0 \ \ . \ 10^{-3}$ | $6·0 \ . \ 10^4$ |
| ,, | . | . | 0·01943 | 0·05 | 0·08 | $7·0 \ \ . \ 10^{-3}$ | $4·3 \ . \ 10^4$ |
| Oxalate | . | . | 0·01884 | 0·05 | 0·2 | $2·26 \ . \ 10^{-3}$ | $3·1 \ . \ 10^4$ |
| Phthalate | . | . | 0·00471 | 0·025 | 0·096 | $1·13 \ . \ 10^{-2}$ | — |

Owing to variations in the concentrations of KCNS and KI, the constants $k'$ and hence the inferred constants $k_S$ and $k'_{OH^-}$ are not quite comparable, but, neglecting this small effect, it is seen that from experiments in each buffer approximately the same value of $k'_{OH^-}$ is obtained. This is good additional evidence in favour of the view that the speed of a part of the reaction is proportional to [OH⁻] (or inversely proportional to [H⁺]). Further, it will be observed that in phosphate and acetate buffers $k_{OH^-}$ increases with increasing salt concentration, that is, with increasing ionic strength, the effect being particularly marked in phosphate buffers. This is to be regarded as a primary or secondary salt effect, or, indeed, it is probably compounded of both.

The values of $k_S$ given in the table depend on the buffer ; they increase as the $K_A$ of the buffer acid decreases. They seem also to be slightly dependent on the salt concentration, increasing somewhat with decreasing [salt]. This may also be ascribed to a kinetic salt effect, or alternatively it may perhaps be due to a residual catalytic effect by water; that is, $k'$ might be made up of three terms, $k_S$ [Salt] $+ k_{OH^-}$[OH⁻] $+ k_{H_2O}$, the last term having a small value.

According to Brønsted, $k_S$ is a function of $K_A$ of the form

$$k_S(nK_A)^x = G \qquad . \qquad . \qquad . \qquad . \quad (4)$$

in which $G$ and $x$ are constants, and $n$ is a statistical factor having the values 1 for acetic acid and phosphoric acid (2nd ionisation constant) and 2 for phthalic and oxalic acids (2nd ionisation constants). Using the values :

| | Oxalate. | Acetate. | Phthalate. | Phosphate. |
|---|---|---|---|---|
| $k_S$ | $2 \cdot 26 \cdot 10^{-3}$ | $6 \cdot 0 \cdot 10^{-3}$ | $1 \cdot 13 \cdot 10^{-2}$ | $1 \cdot 36 \cdot 10^{-1}$ |
| $nK_A$ | $2 \times 7 \cdot 1 \cdot 10^{-5}$ | $1 \times 1 \cdot 8 \cdot 10^{-5}$ | $2 \times 4 \cdot 0 \cdot 10^{-6}$ | $1 \times 8 \cdot 8 \cdot 10^{-8}$ |

a plot of log $(nK_A)$ against log $k_S$ yields a straight line, from which we obtain $x = 0 \cdot 58$ and log $G = -4 \cdot 90$. Equation (4) with these values of $G$ and $x$ may be used to calculate the value of $k_{OH^-}$. With $K_A$ for water equal to $10^{-14}/55 = 1 \cdot 8 \cdot 10^{-16}$, we obtain log $k_{OH^-} = 4 \cdot 23$, which, considering the extent of extrapolation, is in fair agreement with the mean of the observed values in Table VII. of log $k_{OH^-} = 4 \cdot 73$. This concordance shows that that part of the reaction whose speed is proportional to [OH⁻] has the same mechanism as that of the remaining portion, being a reaction catalysed by OH⁻ ions (and not a reaction whose rate-determining step involves a reactant like HOI with concentration proportional to $1/$[H⁺]) in the same sense as the latter is a reaction catalysed by Ac⁻, $HPO_4^{--}$, Ox⁻⁻, or Ph⁻⁻ ions.

Finally, a few experiments at the higher temperature 30° have been made to determine the temperature coefficient. For the reaction in an acetate buffer, a temperature coefficient (between 20° and 30°) of 4·10 was obtained, while in phosphate buffers two experiments gave 3·90 and 4·00. Taking these to be independent of the buffer employed, we have a mean temperature coefficient of 4·0 for the reaction corresponding to a critical increment of 24,500 cals.

## Experiments in Unbuffered Solutions.

Kinetic experiments carried out in absence of a buffer or in very dilute solutions of strong acids (in which therefore the acidity increases rapidly as the reaction progresses) show that the kinetics differ markedly from
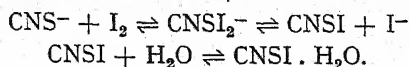
that in buffered solutions. In the first place the velocity of reaction is much lower; further, the rate is proportional not to $[\varSigma I_2]$ but probably to $[\varSigma I_2]^2$ and it appears to be inversely proportional to $[H^+]^2$ and approximately inversely proportional to $[I^-]^4$. Finally, the reaction under these conditions has the very high temperature coefficient of about 10. As the experiments are only of a preliminary nature and afford insufficient basis for generalisations, we may refrain at present from presenting them in detail. A number of experiments have also been carried out under conditions such that the reaction possesses a character intermediate between that in these unbuffered solutions and that in the buffered solutions previously considered. This is the case in acetate buffers in which the ratio $[HAc]/[NaAc] < 1$, the reaction then tending to approximate more and more to the non-buffered reaction the higher this ratio becomes, *i.e.*, with increasing acidity. Their main characteristics may be summarised as follows: (1) With constant $[NaAc]$ (for example $[NaAc] = 0.04$) and increasing $[HAc]$, the rate falls more and more from that inferred from the linear relationship which holds on the alkaline side of $pK_a$. (2) With increasing ratio $[HAc]/[NaAc]$ the reaction tends to become bimolecular with respect to $[\varSigma I_2]$ and (3) its rate becomes more dependent on $[I^-]$, that is from being proportional to $1/[I^-]^2$ it tends to become proportional to $1/[I^-]^3$ or $1/[I^-]^4$. For the reaction in phosphate buffers on the acid side of $pK_2$, the first statement, as we have seen, holds equally, but the applicability of statements (2) and (3) has not been tested.

## Discussion.

The results given above show that the reaction between $CNS^-$ and $I_2$ is of complex character. Under no conditions that we have studied is a simple kinetic equation obeyed. On the other hand, deviations from the kinetic equation $\dfrac{dx}{dt} = k'\dfrac{[\varSigma I_2][\varSigma KCNS]}{[I^-]^2}$ in buffered solutions on the alkaline side of the $pK_a$ of the buffer are not very serious, and the results show conclusively that under these conditions the rate-determining step in the change is one catalysed by bases, such as $OH^-$ ions, $HPO_4^{--}$ ions, etc. It is possible that the failure of the above equation to reproduce the kinetics with exactness is connected with the formation of complexes in solutions containing $CNS^-$, $I^-$, and $I_2$. Distribution experiments carried out in this laboratory by Messrs. D. A. Harper and R. S. Jobin using $CCl_4$ as the second phase have shown that $CNS^-$ and $I_2$ combine to form $CNS . I_2^-$. At $25°$ they obtained the value

$$K = [CNS^-][I_2]/[CNS . I_2^-] = 0.009,$$

corresponding to strong complex formation. Though the introduction of this into the reaction kinetics will not account for the observed deviations from the above kinetic equation, it is possible, in view of the marked tendency of compounds containing the $CNS$ group to form complexes, that in solutions containing $I^-$, $I_2$ and $CNS^-$, other complexes exist besides $I_3^-$ and $CNSI_2^-$, and that these might account for the observed deviations. It is of course possible that these discrepancies are due to more fundamental causes, but for the present they may best be ascribed to some secondary effect such as the one suggested. In this case, the simplest interpretation of the reaction kinetics would appear to be the following mechanism:

$$CNS^- + I_2 \rightleftharpoons CNSI_2^- \rightleftharpoons CNSI + I^-$$
$$CNSI + H_2O \rightleftharpoons CNSI . H_2O.$$

Rate-determining step : (catalysis by bases)

$$CNSI \cdot H_2O + Ac^- \rightarrow CNI + HAc + SOH^- \text{ (or } H^+ + SO^{--})$$
or $$CNSI \cdot H_2O + OH^- \rightarrow CNI + H_2O + SOH^- \text{ (or } H^+ + SO^{--})$$
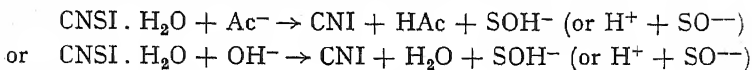
followed by rapid oxidation of $SOH^-$ (or $SO^{--}$) by iodine (or $HIO$) to sulphate.

For the reaction (a) in absence of a buffer and (b) in buffers on the acid side of $pK_a$, further work is necessary before discussion can usefully be made. There is, however, one feature of the reaction under conditions (b) to which attention should be drawn, viz. that the mechanism operating within the alkaline range of the buffer is now suppressed. It is not clear why this should be so ; the effect appears to be a specific effect of the acid constituent of the buffer (HAc, $KH_2PO_4$), whose retarding action is probably due to interaction with the complex $CNSI \cdot H_2O$ which is normally involved in the rate-determining step of the process.

## Summary.

The kinetics of the reaction between potassium thiocyanate and iodine in various buffers have been investigated. The reaction exhibits basic catalysis but is of complex character. A possible mechanism has been suggested.

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# SOME APPLICATIONS OF THE TRANSITION STATE METHOD TO THE CALCULATION OF REACTION VELOCITIES, ESPECIALLY IN SOLUTION.

BY M. G. EVANS AND M. POLANYI.

## I. Introduction.

One of the main objects of this discussion will be to consider the influence of pressure on the velocity of chemical reactions in solution.

Early experiments on the influence of pressure on chemical reactions established the fact that, in certain cases, the velocity of reaction could be profoundly affected. At first it was thought that the influence of pressure could be attributed to secondary effects, which, in their turn, influenced the rate of reaction. Moesveld and de Meester[1] give an explanation based on the change of association of the solvent (aqueous alcohol), which may be applicable in special cases. The extensive work of Cohen[2] and his collaborators, however, removed to some extent

[1] Moesveld and de Meester, *Z. physik. Chem.*, 1928, **139**, 169.
[2] Cohen, *Problems in Piezochemistry*, The Graw Hill Book Co., 1926.

the difficulties connected with these secondary effects, and led to the conclusion that pressure exerts a specific influence on the reaction velocity.

Bridgman,[3] in his review cites further cases, but offers no theoretical explanation. The more recent paper on organic reactions in the liquid phase of Fawcett and Gibson,[4] reports the large increase in reaction velocity which may occur on increasing the pressure which has given rise to this theoretical treatment. Fawcett and Gibson offer a number of suggestions, among them one we consider very essential. They say : " The velocity would also be influenced by pressure if the potential energy gained by the system as a result of the isothermal compression is available as part of the activation energy necessary for reaction." In the following discussion we shall develop the theory of a pressure effect along these lines. Mackeen Cattell,[5] in the discussion on " Factors Determining the Speed of Chemical Reactions," refers to the work of Fawcett and Gibson, and mentions the effect of pressure on muscle action.

The present paper outlines a theoretical treatment of reaction velocities in general, by means of which one can foresee the changes in reaction velocity which the application of high pressure may bring about. This is not a complete statement of the effect of pressure on reaction velocity, and the main effects which we are here considering may indeed be overshadowed by such effects as Moesveld and Meester have discussed.

We shall consider the influence of pressure on chemical reaction velocity as a special case of a more general treatment which we are developing. The ideas and methods used in this treatment are not new. The calculation of reaction velocity by this method, which might be called the method of the transition state, has been foreshadowed in earlier work,[6] and was first worked out in a complete form by Tolman.[7] Practical application of this method has been made by Wigner and Polanyi,[8] and a new presentation with specific reference to the potential energy surfaces to which this present work is most closely related, has been given by Wigner and Pelzer,[9] and by Eyring.[9a] It seems worth while to make this method more specific and to seek to extend its application.

The application of the method should show that the pressure dependence of the rate of a chemical reaction may yield as valuable information as to the *density* of the transition state, as does the temperature dependence for the determination of its *energy*. Moreover, other properties such as dielectric polarisability, dipole moment, magnetic susceptibility or alternatively the electric or magnetic field of the transition state, could be determined in principle, but in these cases experimental realisation is as yet uncertain or entirely lacking.

[3] Bridgman, *The Physics of High Pressures :* Bell & Sons, 1931.
[4] Fawcett and Gibson, *J. Chem. Soc.*, 1934, 386.
[5] Mackeen Cattell, *Proc. Roy. Soc.*, 1934, 116B, 185-207.
[6] Polanyi, see reference [10]. Herzfeld has also outlined the method in his book, *Kinetische Theorie der Warme*, 1925 ; Müller-Poullets Handbuch d. Physik. Z. Aufl.
[7] Tolman, *Statistical Mechanics Chemical Catalog Co.*, 1927.
[8] Wigner and Polanyi, *Z. physik. Chem.*, 1928, 139, 439.
[9] Pelzer and Wigner, *Z. physik. Chem.*, 1932, 15B, 445.
[9a] Eyring, *J. Chem. Physics*, 1935, 3, 107. This communication appeared when the present paper was almost completed.

This communication also attempts a derivation of the collision factor, (*a*) for complicated molecules, (*b*) for reactions in solution (in general), and (*c*) for slow reactions in particular.

## 2. The Method.

Consider an energy barrier between the initial and the final states of the reaction system ; chemical reaction will consist in the system passing over the top of this energy barrier from the initial to the final states. The system will be one-dimensional in the sense that, when the system is at the top of the barrier, the variation, which corresponds to a decrease in the potential energy, should be one-dimensional. It is important to note that this dimension will, in general, be a function of all the co-ordinates, but might itself be used as a co-ordinate.

In former publications, a line representing what has been termed the " reaction path " has been introduced into the diagrams of the potential energy surface for a reaction ; the co-ordinate considered here is a line tangential to the reaction path at the top of the potential energy barrier. This co-ordinate we will call $l$.

At the top of the potential energy barrier the system can possess translational and rotational motion in six dimensions and, moreover, can move in the dimension $l$, giving in all a total of seven dimensions. Every other change in the co-ordinates will involve an increase in the potential energy of the system in every other dimension, and so the system will be in a potential hollow of $3n - 7$ dimensions, thus conferring $3n - 7$ characteristic vibration frequencies on the system in the transition state at the top of the barrier.

We define the probability of the transition state by defining an infinitesimally thin layer of phase space of thickness $dl$ with faces perpendicular to the dimension $l$ and extending to infinity in all dimensions other than $l$. The probability of the state is the probability $P$ of a state independent of $l$ multiplied by $dl$, that is $P . dl$. All the forces are assumed to give rise to harmonic oscillations, otherwise we cannot express the probability of such a state. All systems whose representative points lie within this layer are considered the transition state. Every time a representative point passes in either direction across the layer defined above, it leads to the completion of chemical reaction in that direction. This implies that there must be a complete dissipation of energy when a system leaves the layer of thickness $dl$ and we can, therefore, exclude from consideration those reactions where the dissipation, or the accumulation, of energy becomes the rate determining factor. The non-dissipation of energy on leaving the transition state would introduce the possibility of the representative point returning to the transition state, without having passed into the final state ; in the reactions we wish to consider by this method, all representative points leaving the transition state should pass through the initial or final states before returning to the transition state, so that we can state that a representative point leaving the layer leads to chemical reaction in that direction.

We postulate the further condition that the products of the reaction may not take part in the initial state, that is, as reactants. Such a condition excludes chain reactions.

The systems we can study by this method are quite general, within the restrictions laid down, and will include gas, liquid and heterogeneous

reactions, but, although no further essential restrictions are necessary, the practical restrictions may be very complicated in any particular case.

**The Life Period.**

When an equilibrium exists between the initial and final states of the reaction system, then the probabilities of transition from the layer of thickness $dl$ in the forward and reverse directions are independent of each other and we can, therefore, calculate the reaction rate in either direction from the probability of the transition state and the life time of the representative point, that is, the time required for the representative point to cross the layer in the direction of reaction.

At complete equilibrium between the initial and final states of the reaction, the representative points in the transition state will be made up of those arriving from the initial and the final states of the equilibrium ; *half* the number of representative points in the transition state at equilibrium will give the reaction velocity in one direction or the other. The number of representative points arriving in the transition state when the equilibrium is established between the initial and final states, will, of course, be proportional to the concentrations, considered in the initial and final states.

The reaction velocity will be given by

$$\text{Reaction Velocity} = \frac{1}{2} \cdot \frac{\text{Probability of Transition State}}{\text{Life Time}}.$$

We have, however, shown that the probability of the transition state is given by $P \cdot dl$, and we define the life period of the representative point in the transition state as $dl/v$, where $dl$ is the thickness of the layer and $v$ is the average velocity of the representative point at the top of the barrier in the direction of the $l$ dimension. The reaction velocity, then, can be written

$$\text{rate of reaction} = \tfrac{1}{2} P \cdot v,$$

and it is to be noticed that the thickness $dl$ chosen to define the transition state does not enter into the expression.

Employing thermodynamic language, we can speak of an equilibrium between the initial and the transition state. We will define an equilibrium constant $K$ such that $K \cdot dl$ is proportional to the probability of the transition state $P \cdot dl$. This equilibrium constant is related to the true equilibrium constant $K$ for the reaction, and to the corresponding equilibrium constant for the equilibrium between the final and transition states, by the expression $(K_1 \cdot dl)/(K_2 \cdot dl) = K$ and similarly the reaction velocity constants of the forward and reverse reactions are given by

$$k_1 = \tfrac{1}{2} K_1 dl \cdot v/dl = \tfrac{1}{2} K_1 v$$
$$k_2 = \tfrac{1}{2} K_2 dl \cdot v/dl = \tfrac{1}{2} K_2 v$$

and hence

$$\frac{k_1}{k_2} = \frac{K_1}{K_2} = K.$$

In these expressions the collision factor, as usually expressed by gas kinetic expressions, has disappeared, and the kinetic magnitudes have

been replaced by the thermodynamic probability of the collided state.[10]

## Crossing of Levels.

The transition state method has hitherto only been considered for adiabatic processes, *i.e.*, those in which the energy surface as a function of the co-ordinates has a single value. This also holds, for all practical purposes, in cases where we have crossing of energy surfaces, if the separation due to splitting of the degenerate states is of the order of $kT$ or more, and the curvature of the top of the energy barrier is only slight, while the masses of the particles are large. For light masses, such as hydrogen and deuterium, the statistical probability must be calculated according to the principles outlined by Wigner[11] which will result in the appearance of tunnelling effects.

The treatment becomes more difficult if the splitting is $< kT$, since in this case the particles will have a considerable probability of moving either on the one surface or the other, and the probability of transition from one surface to the other will be small.

It is interesting to note that the transition from one curve to the other will be more probable for deuterium D than for protium H, since the heavier mass involves a reduced impulse at equal temperatures. We have here a factor of the order of $\sqrt{2}$ tending to make D *more reactive* than *H*.

## 3. General Principle.

We now consider the probability of the transition state and the variation of this probability with the change of an environment variable. We can express this, since $K$ is an equilibrium constant, in a general way by an expression of the form

$$\frac{d \log K}{df} = \frac{\alpha - \alpha'}{RT} \qquad . \qquad . \qquad . \qquad . \qquad (\text{i})$$

where $K$ is the equilibrium constant, as defined, between the initial and transition states and is proportional to the probability of the transition state, and $\alpha$ and $\alpha'$ are factors such that $(\alpha - \alpha')f$ is the energy change in the system in passing from the initial to the transition states.[12] If $f$ is taken to mean the temperature, then $(\alpha - \alpha') = Q/T$ (activation energy over temperature) and equation (i) becomes identical with Arrhenius' equation. The case with which this paper is most concerned is $f = \pi$ (hydrostatic pressure). In this case (see section 4) $\alpha - \alpha' = \Delta V$, *i.e.*, the volume change accompanying the formation of the transition state.

Obviously a great number of other variables might be taken for $f$, some of which we have mentioned in the introduction. The most

[10] The substitution of the collision number by the statistical probability of the collided state (*Fahrzustand*) has been presented by one of the authors (*Z. physik.*, 1920, **1**, 90) in a paper which applied the transition state method, using the concepts of the old quantum theory. It has been pointed out (*Z. Electrochem.*, 1920, **62**, 228) that the method overcomes the difficulty arising when one introduces the Arrhenius equation into the equilibrium constant, since it leads to the exact form of the reaction isochore. This difficulty has been recently emphasised by Rodebush (*J. Chem. Physics*, 1933, **1**, 440).

[11] Wigner, *Physic. Rev.*, 1932, **40**, 749.

[12] A qualitative indication of this relation is to be found in *Z. Electrochem.*, 1929, **35**, 561.

notable form of actually introducing and varying the factors of environment is by letting the reaction proceed in solution and changing the solvent either continuously, by adding other solutes or discontinuously by replacing it altogether.

Such changes would take effect on the energy of interaction between solvent and solute in various generally known ways, connected on the one hand with the electrical properties and the van der Waals forces of the solute and solvent.    When the effective changes in the solute (the variables $f$) are known, the application of equation ($1$) to the observed changes in reaction velocity will yield constants $\alpha$ and $\alpha'$ containing the magnitudes of the transition state already mentioned (*viz.* dielectric polarisability, dipole moment, magnetic susceptibility, electric or magnetic field).

In this paper we restrict ourselves to the discussion of one case of the influence of solvent, which arises in connection with the treatment of the effect of hydrostatic pressure.

## 4. Application to the Influence of Pressure.

In this case the general equation will have the form

$$\frac{d \log K}{d\pi} = \frac{\Delta V}{RT} \qquad . \qquad . \qquad . \qquad . \quad \text{(iia)}$$

where $\pi$ represents the hydrostatic pressure and $\Delta V$ is a volume change. The volume change $\Delta V = V_1 - V_2$ is the difference in volumes in the initial and transition states.    $V_1$ will be the volume of a solution containing a mol of the reactants in the initial state and $V_2$ the volume of the same solution when all the molecules of the initial state have been changed into the transition state.    This volume change will be made up of two factors :—

(a) Changes in the molecules themselves as they pass from the initial to the transition state ; in certain cases we can approximate to this change in configuration.    The transition state can be represented by the equation

$$\begin{array}{ccc} \text{A} + \text{B} + \text{C} \ldots & \rightarrow \quad (\text{ABC} \ldots) & \rightarrow \quad \alpha + \beta + \gamma \ldots \\ \textit{Initial State.} & \textit{Transition State.} & \textit{Final State.} \end{array}$$

and is made up of all the atoms taking part in the reaction.    The reacting molecules have now lost their identities, and have become fused into a new molecular species.    In this new molecular species, the transition state will have a definite configuration and a definite molecular volume.    We can illustrate the kind of volume change which will be operative by a consideration of the reaction between hydrogen and iodine molecules to form hydrogen iodide.    Ekstein [13] and one of us have calculated for this reaction the potential energy surface, from which the approximate configuration of the atoms in the transition state may be determined.    In the transition state all the atoms lie in a straight line joining their centres, and the dimensions are
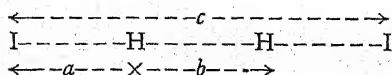


[13] Ekstein and Polanyi, *Z. physik. Chem.*, 1932, **15B**, 334.

$a \sim 2 \cdot 0$ to $2 \cdot 2$Å. ; $b \sim 0 \cdot 75$ to $0 \cdot 85$ Å. ; and $c \sim 4 \cdot 75$ to $5 \cdot 05$ Å.   The intermolecular distances of the reacting hydrogen and iodine molecules are respectively $0 \cdot 75$ Å. and $2 \cdot 66$ Å.   The volume change considered in this section can be represented diagrammatically by drawing volumes of influence round the reacting molecules in the initial state and in the transition state (Fig. 1).   An estimate of the volume of the latter can be obtained by constructing a cylinder of cross section equal to that of the iodine molecule, with hemi-spherical ends of radius equal to the iodine molecule, round the transition configuration.   If an estimate of the volume change is made in this way it is found that a decrease in volume of about 20 ccs. accompanies the change from the initial to the transition state.*

(**b**)  A change in the nature and strength of the forces exerted by the system on the molecules in the solvent in passing from the initial to the transition state.   If the forces between the transition state and the solvent exceed the corresponding forces for the initial state, then the formation of the transition state will be accompanied by a contraction of the solvent.   This contraction forms part of $\Delta V$, which thus consists



Initial state.          Transition state.          Final state.
FIG. 1.
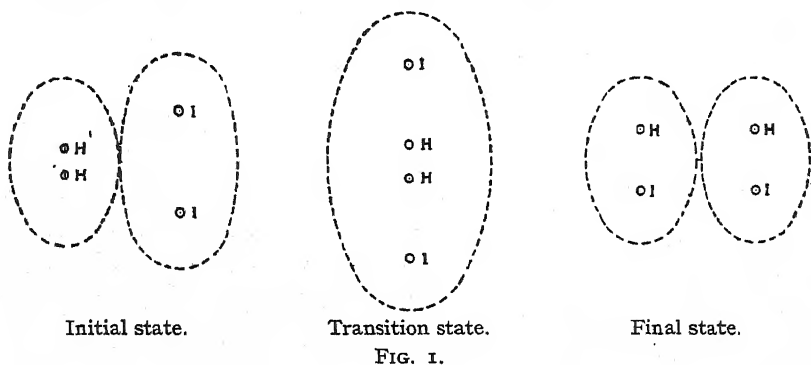
of two terms, $\Delta_1 V$ determined mainly by the configuration of the transition state, and $\Delta_2 V$ determined by the interaction between solvent and transition state

$$\frac{d \log K}{d\pi} = \frac{\Delta_1 V}{RT} + \frac{\Delta_2 V}{RT} \qquad . \qquad . \qquad . \quad \text{(ii}b)$$

One example of the second factor has been explicitly discussed [14] in the case of organic substitutions of the type $X^- + RY \rightarrow XR + Y^-$.   The transition state can be represented as a complex $X^- \; RY$ or $XRY^-$. The electrostatic forces acting from such a complex on a solvent are smaller than those from the particles $X^-$ and $RY$ in the initial state. The reduction is caused by the molecule $RY$ screening off the solvent on one side of $X^-$ in the transition state.

In consequence of this effect, the solvent should be released from

* Another and probably more convincing method of calculating the volume change in passing to an associated state would be to take the molecular volumes for the molecules in the association of two isoprene molecules to one dipentene molecule.   A computation of this from the densities yields isoprene mol. vol. $\sim$ 100.   Dipentene mol. vol. $\sim$ 157—a change from 200 ccs. in the initial state to 157 ccs. in the associated state—a decrease of 43 ccs.

[14] See Ogg and Polanyi, *Trans. Far. Soc.*, 1935, **31**, 604, also a recent paper by Hughes and Ingold, *J. Chem. Soc.*, Feb. 1935.

some of the contraction caused by the electrostatic forces of the initial state (*i.e.*, $\Delta_2 V$ should have a negative value) and the pressure coefficient corresponding to the second term in equation (ii*b*) should be negative (*i.e.*, have a retarding influence).

It has been mentioned in previous discussions that this process of partial desolvation of an ion reacting with an organic molecule leads to a retarding influence of the solvation energy, *i.e.*, the reaction goes more slowly in solvents of higher dielectric constant. We can express this in an approximately quantitative form derived from equation (I). Let us suppose the dielectric constant to be changed continuously and set $f = \epsilon$ (dielectric constant), then

$$\frac{d \log K}{d\epsilon} = \frac{F_1^2 - F_2^2}{RT}$$

where $F_1^2$ and $F_2^2$ are integrals of the form $\int dF d\tau$ with $F$ as the electrostatic field strength and $d\tau$ extended over the space co-ordinates, $F_1^2$ referring to the initial and $F_2^2$ to the transition state.

Again, supposing $(F_1^2 - F_2^2)$ to remain constant for different solvents. We then have in a pair of solvents A and B.

$$\frac{\log K_A - \log K_B}{\epsilon_A - \epsilon_B} = \frac{F_1^2 - F_2^2}{RT}.$$

## Some Reactions with Contracted Transition States.

In reactions in which a change of valence, or the opening of double bonds occurs, we should expect a pronounced acceleration by pressure. As an example of such a reaction we may take the combination of hydrogen and carbon monoxide to give formaldehyde. The activation energy of such reactions can be illustrated by Fig. 2.

Curve *a* represents the change in potential energy when the formaldehyde breaks up into hydrogen and an excited carbon monoxide molecule in which the carbon is tetravalent.
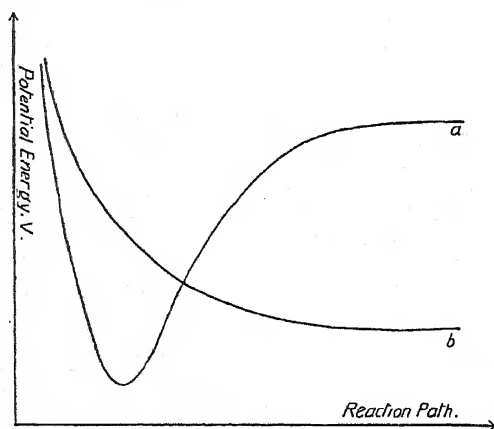


FIG. 2.

Curve *b* represents the compression curve between hydrogen and a normal carbon monoxide molecule. The reaction between hydrogen and carbon monoxide occurs when the hydrogen and carbon monoxide are compressed together to such a point that the configuration and the energy of the system is equal to that of the formaldehyde system when the $\begin{smallmatrix} H \\ H \end{smallmatrix}$CO is extended. It is clear that, since the transition state is a

compressed state, we should expect reactions of this kind to be acceler-
ated by an increase in pressure.

Polymerisation changes provide examples of other reactions of this
type. These also, in general, involve an analogous change in valence
or opening of a double bond. For example, the change from isoprene
to dipentene :

$$
\begin{array}{ccc}
CH_3 & & CH_3 \\
| & & | \\
C & & C \\
\end{array}
$$
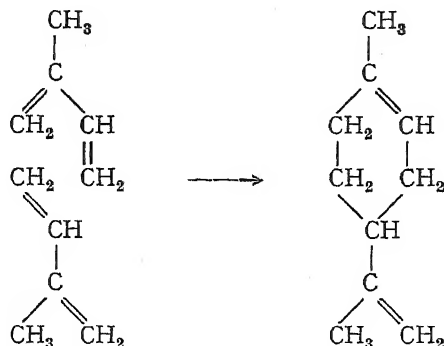
Such reactions will, in general, then, be increased in velocity by an
increase in pressure, for it is reasonable to suppose that, as in the case
of carbon monoxide and hydrogen, the transition state will possess a
volume intermediate between that of the initial and final states of the
system. All cases of polymerisation which have been examined show
an increased reaction velocity under high pressures.

It has frequently been surmised that reactions which are accom-
panied by a contraction should be accelerated by pressure. The above
discussion shows that such is only to be expected when the density of
the transition state is intermediate between that of the initial and
final states. This will not generally be true, and one readily under-
stands, therefore, why the *cis*-trans isomerism of fumaric acid (a
reaction in which a contraction between the initial and final states is
involved) is not accelerated by pressure, since in this case the transition
state is probably one in which the C—C linkage is extended and which
therefore has a lower density than either the initial or final states.

Eyring, Sun and Sherman[15] have recently discussed the activation
energy of the process $H_2 + \ \rangle C = C \langle \ \rightarrow \ \rangle CH - CH \langle$. Follow-
ing their treatment, one can readily confirm our assumption that the
transition state of such reactions has a density intermediate between
that of the initial and final states.

The fact that these authors do not take the view implied above,
that the reaction involves an electron switch (*i.e.*, the system is formed
by an aggregate of two states) but consider the reaction as a four
electron problem of London's theory, makes no difference to the con-
clusion that the volume of the transition state is intermediate between
that of the initial and final states.

## 5. Order of Magnitude of the Pressure Effect.

Equation (2) as applied to the reaction $H_2 + I_2 \rightarrow 2HI$ yields an
acceleration of the reaction velocity by hydrostatic pressure, the order

[15] Eyring, Sun and Sherman, *J. Chem. Physics*, 1935, 3, 49.

of which can be predicted from our calculation of $\Delta_1 V$ in section $4a$. Assuming for the molar volumes of $H_2$ and $I_2$ the respective values 25 c.c. and 51·4 c.c., we find $\Delta_1 V \sim 20$ c.c. and

$$\frac{d \log K}{d\pi} \sim 0·8 \times 10^{-3} \text{ per Atm.}$$

for ordinary temperatures $(T = 300)$.

This is actually the observed order of the strong accelerations in reactions of the type $>N + RI \rightarrow >NRI$. In section 9 we shall show that the " fused " molecule representing the transition state of such reactions (belonging to the group of " slow " reactions) has a configuration closely approaching that of the final state. This is an association product and has therefore a much smaller volume than the initial reactants. It seems reasonable to assume that the term $\Delta_1 V$ arising from this reduction in volume should have about the same value as that calculated for the formation of the fused state
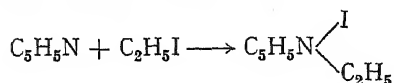
$$I- - - - - -H- - - - - -H- - - - - -I$$
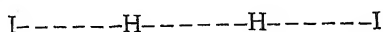
in section $4a$. This would explain the magnitude of the observed acceleration by pressure. The contribution of the term $\Delta_2 V$ is probably small, since the reaction is non-ionic in the first phase.

Saponification of a carbon halogen linkage by $OEt^-$ or $OH^-$ (a reaction of the type discussed in section $4b$) should involve a partial desolvation of the ion in the transition state. A decrease of reaction velocity by pressure should be expected on this account. Actually an increase in reaction velocity was observed in the case of

$$C_2H_5ONa + C_2H_5I \longrightarrow C_2H_5O\ C_2H_5 + NaI,$$
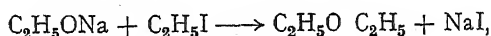
but this was much smaller than for

$$C_5H_5N + C_2H_5I \longrightarrow C_5H_5N\begin{matrix} I \\ \diagdown \\ C_2H_5 \end{matrix}$$

The measurement of the temperature coefficient seems to indicate that the activation energy is unchanged, but that there is an increase in collision number. This increase in collision number might be due to second order effects discussed in the next section. A theory of the collision number under pressure could be obtained by the treatment outlined in section 10, if a correct theory of the solubility of gases were available.

In the next section we shall show that equation (2) leads us to expect an exponential dependence of reaction velocity on pressure ; the verification of the conclusion given there yields additional evidence that equation (1) contains the relevant functions underlying the pressure effect. The exponential relation affords a method of separating the second order effects from the primary ones.

We wish to emphasise that this theory is only applicable when the solvent remains unchanged by pressure, and that in comparison with experiment such disturbing influences should be kept in mind.

## 6. The Pressure Effect over a Wider Range.

If the differential equation can be integrated on the assumption of a constant value of the term $\Delta V$, the general pressure effect would have the form of an exponential relationship $K = K_0 e^{\pi \Delta V / RT}$. This assumption is supported by the results of Fawcett and Gibson on the rate of formation of cetyl-pyridinium halides, the results on the bromides giving particularly good exponential relationship.*

The integrated expression, however, will in general be inexact, because of the change of $\Delta V$ with pressure. This could be determined if we knew the compressibilities of the initial and the transition states.



FIG. 3.

We have received a private communication [16] of some recent results on the influence of pressure on the reaction

$$C_5H_5N + C_2H_5I \rightarrow C_5H_5N{\Big\langle}{\phantom{a}}^{I}_{C_2H_5}$$
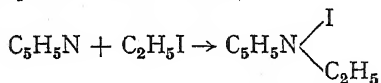
The form in which the reaction velocity depends on temperature and pressure in these experiments is not in agreement with equation (ii) when integrated under the assumption of a temperature and pressure independent $\Delta V$. We leave the question of this discrepancy for later consideration.

The integrated equation, taking account of the compressibility of the initial and transition states, would be

$$\log K_1 - \log K_2 = \frac{a}{RT}\int_{\pi_1}^{\pi_2} V_a d\pi + \frac{b}{RT}\int_{\pi_1}^{\pi_2} V_b d\pi \ \ldots \ - \frac{t}{RT}\int_{\pi_1}^{\pi_2} V_t d\pi,$$

where $V_a \ V_b \ \ldots$ are the molal volumes of the constituents of the initial state and $V_t$ the molal volume of the transition state. It can be seen from this equation that the compressibility of the initial and

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* The tangents to the reaction curves in the very early stages of reaction have been used as a measure of the velocity.

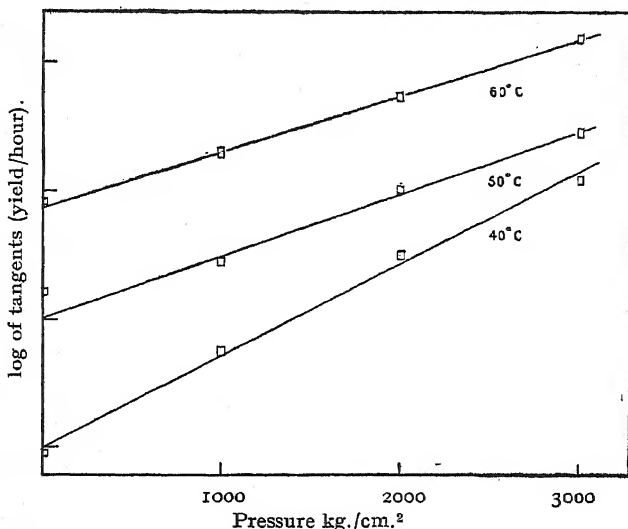[16] E. W. Fawcett, R. O. Gibson and M. V. Perrin, *Proc. Roy. Soc.*, 1905, A150, 223.

transition states may, in certain cases, enter in as a second order correction of the primary process we have considered.

In deducing the general equation $\dfrac{d \log K}{df} = \dfrac{\alpha - \alpha'}{RT}$ we have assumed that the velocity $v$ of the representative point is independent of the parameter $f$. This will, in general, be the case, since the reduced mass of the representative point will not be liable to changes under the influence of changes in environment.

The exact form of the expression is $\dfrac{d \log k}{df} = \dfrac{\alpha - \alpha'}{RT} + \dfrac{d \log v}{df}$. The second term can only be evaluated if we know something of the change of the reduced mass with changes of the parameter $f$. The relation which expresses the reduced mass $M$ in terms of the potential energy $\phi$ along the $l$ co-ordinate is

$$\frac{d\phi}{dl} = - M\ddot{l}.$$

The existence of these relationships should be kept in mind, especially when integrating the general equation over a wide range of varying conditions. We will now point out some of the consequences of this method of treatment, and the ways in which it may be used.

### 7. Preliminary Equilibria and Reaction Velocity.

The equation $k = \frac{1}{2}Kv$ is unqualified by any preliminary equilibria arising between the initial state and the transition state. The only requirement is that the states involved in such preliminary equilibria should have a high probability as compared with that of the transition state. This condition is necessary to exclude a return of the representative point to the transition state before it has passed into the initial state (see section 2). In saying this we have in mind numerous cases where preliminary equilibria have been introduced to explain the failure of some kinetic expression; such a procedure is clearly unjustified. This conclusion is very obvious when we are dealing with homogeneous reactions, but it is not so simple in the case of heterogeneous reactions, where indeed all the current treatments are based on a consideration of the preliminary equilibria of the reactants with the adsorbents. We cannot explore this further here, so we only remark that the effects of preliminary equilibria are to be dealt with as changes of $K$ caused by the presence of adsorbed substances.

### 8. Internal Degrees of Freedom and Reaction Velocity.

We now consider whether, in calculating the rate of *bimolecular* reactions, we are justified in introducing the internal degrees of freedom into the formula relating the number of collisions with total energy greater than a critical amount. In this formula it is assumed that the energy possessed by the reacting molecules in their internal degrees of freedom is capable of contributing to the provision of the necessary activation energy.

On this assumption the velocity constant of a bimolecular reaction can be expressed

$$k = \frac{2\nu_1 \nu_2 \sigma_{12}^2}{\Gamma(s_{1/2} + s_{2/2} + 2)} \left\{ 2\pi \frac{(m_1 + m_2)}{m_1 m_2} kT \right\}^{1/2} \left( \frac{\eta_0}{kT} \right)^{s_{1/2} + s_{2/2} + 1} e^{-\eta_0/kT} \quad \text{(iii)}$$

where $S_1$ and $S_2$ are the numbers of degrees of freedom in the reacting molecules and $\eta_0$ the activation energy of the reaction.

We do not question the applications of this formula to monomolecular reactions at low pressures, where the rate at which energy is accumulated in the decomposing molecules is rate determining. The use of this formula for bimolecular reactions which has been made in the literature appears, however, to be unjustified, and an altogether different equation for bimolecular reactions between big molecules results from the application of the transition state method. In this treatment the influence of internal degrees of freedom on the velocity of reaction can be obtained from the expression for the equilibrium constant between the initial and transition states.[17]

$$K = \frac{A_t B_t C_t}{A_1 A_2 B_1 B_2 C_1 C_2} \, e^{-E/RT}$$

where $E$ is the difference in energy between the initial state and the transition state. $A_1 A_2 B_1$ . . . represent the partition functions for the various forms of motion of the initial state and $A_t B_t$ . . . those for the transition state. These various partition functions will have the forms : $A_1$, $A_2$ and $A_t$,

$$A_1 = \frac{V(2\pi m_1 kT)^{3/2}}{h^3}, \quad A_2 = \frac{V(2\pi m_2 kT)^{3/2}}{h^3}, \quad A_t = \frac{V(2\pi(m_1 + m_2)kT)^{3/2}}{h^3},$$

where $m_1$, $m_2$ and $(m_1 + m_2)$ are the masses of the initial reacting molecules and the transition state respectively. $B_1$, $B_2$ and $B_t$ are the contributions due to the rotations of the molecules in the initial and transition states

$$B_1 = \frac{8\pi^2(8\pi^3 I_1' I_1'' I_1''')^{1/2}}{h^2}(kT)^{3/2}, \qquad B_2 = \frac{8\pi^2(8\pi^3 I_2' I_2'' I_2''')^{1/2}}{h^2}(kT)^{3/2},$$

$$B_t = \frac{8\pi^2(8\pi^3 I_t' I_t'' I_t''')^{1/2}}{h^2}(kT)^{3/2},$$

where $I_1'$ . . . $I_2'$ . . . $I_t'$ . . . are the moments of inertia of the initial and transition states respectively.

$C_1$, $C_2$ and $C_t$ are the contributions due to the vibrational frequencies of the initial and transition states.

$$C_1 = \prod_{r=1\ldots}(1 - exp(-h\nu_r/kT))^{-1}.$$

If the frequencies are relatively small, so that the exponential term can be written $1 - (h\nu_r)/(kT)$, we can write $C_1$, $C_2$ and $C_t$ as

$$C_1 = \prod_{r_1\ldots}\left(\frac{kT}{h\nu_{r_1}}\right), \quad C_2 = \prod_{r_2\ldots}\left(\frac{kT}{h\nu_{r_2}}\right), \quad C_t = \prod_{r_t\ldots}\left(\frac{kT}{h\nu_{rt}}\right),$$

where $C_1$ and $C_2$ are the continued products over $3n - 6$ vibration frequencies of the initial state, while for $C_t$ we shall have $6n - 7$ terms.

There will be another term in the complete partition function for the

[17] In expressing the equilibrium constant in this way we come to results already presented by Eyring who has given the absolute velocity of certain chemical reactions in terms of partition functions ; *J. Chem. Physics,* 1935, **3,** 107.

transition state, *viz.*, the contribution due to the translational move-
ment of the phase point along the dimension $l$.   This will be a term
similar to the ordinary term for translational motion, but in one dimen-
siononly, *i.e.*, of the form $l \frac{(2\pi MkT)^{1/2}}{h}$, where $M$ is the effective mass of
the transition state along the $l$ dimension.   We can define $M$ in terms
of the generalised co-ordinates of the transition state, and the change
in potential energy.

If $\phi$ is the potential energy, then [18]

$$M\ddot{l} = -\frac{\partial\phi}{\partial l},$$

and the mass $M$ is completely determined by the configuration of the
transition state and the form of the potential energy surface.

We are now in a position to examine the effect on the reaction
velocity of the internal degrees of freedom in the reacting molecules.
For the initial state $C_1 \cdot C_2 = \prod\left(\frac{kT}{h\nu}\right)$ taken over $6n-12$ frequencies, a
contribution of $3n-6$ from each reacting molecule.   The contribution
to the partition function of the transition state will be $C_t = \prod\limits^{6n-1}\left(\frac{kT}{h\nu}\right)$ an
increase of five new vibrational frequencies.   If we assume, in the first
approximation, that the frequencies present in the original molecules
are present with approximately the same values in the transition state,
then, the contribution to the equilibrium constant between initial and
transition state will be of the order of $\prod\limits_{s=1\ldots5}\left(\frac{kT}{h\nu_s}\right)$ over the five new vibra-
tional frequencies.   So that, in the formation of the transition complex,
three translational and three rotational degrees of freedom have dis-
appeared and are replaced by five new vibration frequencies and one
degree of freedom along dimension $l$.   From these approximate con-
siderations it is apparent that the internal vibration energies of the
original molecules do not, in general, enter into the equilibrium con-
stant which determines the velocity of the reaction.   The application
of equation (iii) to bimolecular reactions, therefore, appears to be
unjustified in fact, the effect of large numbers of " degrees of freedom "
in the initial state will probably have the effect of reducing the prob-
ability of the transition state.   A reduction of probability of the
transition state (which is not caused by an increase of its energy) means
a reduction of the reaction velocity in the form of a steric factor.
Whereas we should expect atoms * or molecules involving small
numbers of internal degrees of freedom to react at every collision with
the required activation energy, there will be, in the case of more com-
plicated structures, an added inertia due to the decreased probability
of the associated state.

The reduced probability of the associated product caused by the
complexity of the associating particles must, of course, appear also in
the case of ordinary association equilibria.   Comparing, for example,

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[18] The solution of this in a special case has been contributed by Wigner to a
paper by Eyring and Polanyi ; *Z. physik. Chem.*, 1931, **12B**, 279.
   * Provided of course that there is a sufficiently rapid dissipation of energy.

the equilibrium $2Cl \leftrightarrow Cl_2$ with the equilibrium $2NO_2 \leftrightarrow N_2O_4$ where the associating particles have about equal masses, we find the empirical equations. For the first reaction,

$$\log K - 11{,}800/T = - 1{\cdot}75 \log T - 0{\cdot}93,$$

while for the second case,

$$\log K - 2{,}692/T = - 1{\cdot}75 \log T - 3{\cdot}06,$$

which indicates that the associated state is very much more probable in the case of chlorine, where only two atoms are associating, than in the case of $NO_2$ where many more internal degrees of freedom are involved.

This discussion leads us to the question of the steric factor in chemical reactions in a way somewhat related to that followed by Rice and Gershinowitch.[19] These authors have arrived at a steric factor by a tentative separation of the entropy change for the complete equilibrium into terms relating to the factors independent of temperature for the bimolecular association reaction and for the unimolecular decomposition.

We can deduce from the discussion of the preceding section that the steric factor will be the more effective the greater the complexity of both the reacting molecules and the narrower the restrictions laid upon their relative positions in the transition state. We should expect, then, an especially pronounced effect in cases where two tertiary or quaternary atoms are linked together in the transition state because, in these cases, both the above factors, complexity and restricted position, are operative. The association of triphenyl methyl radicals to form hexaphenyl ethane is an example of this. We find in fact that, in this case, the degree of association, as given by the equilibrium constant, is especially low as compared with the (theoretical) value of the equilibrium constant for the association of two atoms of the same mass $K$ (Hexaphenylethane) $= 0{\cdot}25 \times 10^{-4}e^{10{,}500/RT}$; $K$ (atomic) $\approx 6e^{10{,}500/RT}$.

## 9. " Slow Reactions."

In studying bimolecular reactions in solution Hinshelwood and Moelwyn Hughes [20] have observed that while a large group of reactions and collision factors correspond about to the collision factor in the gas phase, another group was characterised by much smaller collision factors. These slow reactions are all processes in which tertiary nitrogen compounds form quaternary complexes with organic halides, the first stage being probably the formation of a pentavalent nitrogen complex. From the above considerations it is easily recognised why such reactions should have a depressed collision factor.

We can assume that in a process such as

$$C_6H_5NR_2 + RI \longrightarrow C_6H_5NR_3I$$
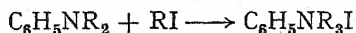
the transition state has a configuration differing from the final state only in that the internuclear distance between the atoms forming the new link is slightly greater than in the final state. For the equilibrium

[19] Rice and Gershinowitch, *J. Chem. Physics*, 1934, **2**, 853.
[20] Moelwyn-Hughes and Hinshelwood, *J. Chem. Soc.*, 1932, 230.

constant $K$ for the formation of such a transition state we have to expect (in analogy to the equilibrium of hexaphenylethane and of $N_2O_4$ as well as on the basis of the theoretical considerations of the preceding section) that the temperature independent factor will be small.    This, together with the equation $k = \frac{1}{2}Kv$ explains the slowness of these reactions.

An alternative hypothesis, which has been discussed by Hinshelwood, might be that the slowness of these reactions is due to a non-allowed transition related to electron switch.    That this is not the explanation of slow reactions is made probable by the work of Hinshelwood and Williams,[21] who have shown that, in a series of homologous reactions, whereas the activation energy changed from one reaction to another the temperature independent factor remains unchanged.

Another argument in the same direction is found by considering the kinetics of the formation and decomposition of hexaphenylethane. A. Wassermann [22] has pointed out that, from the equilibrium constant and the decomposition velocity measured by Ziegler,[23] a rate of formation can be calculated which shows the reaction to be of the " slow " type.    Since, on the other hand, we find that the temperature independent factor of the decomposition has the theoretical [8] value of $10^{13}$, we must conclude that the factor causing the slowness influences only the rate of formation and not the rate of decomposition.    This factor, therefore, cannot be a restriction laid upon the transition probability of an electron switch, since such restriction would be effective in both directions of the reaction.

The assumption we have made that, in the slow reactions, the transition state is near to the final state in configuration, is identical with the assumption implied in the theory of the unimolecular decomposition rate, to which reference has been made above,[8] and finds its direct justification in the fact that the decomposition rate of hexaphenylethane complies with this theory.*

None of the reactions in which Hinshelwood and Moelwyn-Hughes found the collision factor to be " normal " (*i.e.*, having a value corresponding approximately to the collision number of a gas reaction) belong to the type for which our theory postulates a " slow " rate.    These are reactions in which one of the participants is a simple ion.    In the next section we shall outline some considerations as to the collision number of such reactions in which restrictions of the kind prevailing in the slow reactions are absent.

### 10. Reactions in Solutions in General.

The transition state method described here, which can be considered as a generalisation of Brønsted's theory enables one to give a more precise formulation to the " activated complex " method on which that theory is based.
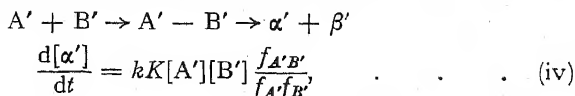
[21] Williams and Hinshelwood, *J. Chem. Soc.*, 1934, 1079.
[22] A. Wassermann.    Communicated in lecture in Manchester, 1934.
[23] Ziegler, *Ann.*, 1929, **473**, 163 ; 1933, **504**, 124, 145.
* As we have already pointed out, the solvent molecules may take part in the transition state and if there is a special orientation of the solvent molecules this will add further restriction on the co-ordinates and will cause a reduction of the probability of the transition state.    Such a decrease in probability will constitute a steric factor.

If we compare the Brønsted equation (iv) and the one given in this discussion (v) for the reaction

$$A' + B' \rightarrow A' - B' \rightarrow \alpha' + \beta'$$

$$\frac{d[\alpha']}{dt} = kK[A'][B'] \frac{f_{A'B'}}{f_{A'}f_{B'}}, \qquad . \qquad . \qquad . \quad (iv)$$

where $k$ is the velocity constant and $K$ is the equilibrium constant for the first step while $f$'s are activities

$$\frac{d[\alpha']}{dt} = Kv[A'][B'] \qquad . \qquad . \qquad . \qquad . \quad (v)$$

two differences become apparent. Firstly, the constant $K$ is not an equilibrium constant in the usual sense, since its dimensions are that of an ordinary equilibrium constant multiplied by cm.$^{-1}$. It becomes equivalent to the usual equilibrium constant if we introduce the mathematical fiction that the co-ordinate $l$ of the transition state is extended to unit length.

The second difference is that the constant $k$ left undefined in the Brønsted equation is, at least in principle, given its absolute value.

The actual evaluation of the constant would lead to a determination of the collision number for reactions in solution. The following discussion indicates how the collision number can be derived.

We consider the components of the reaction in solution to be reacting in the gaseous phase, and the reaction velocity in solution is found, as a function of the concentrations of reactants in solution, by multiplying all the concentrations in the gas phase by their solubilities

$$K' = K \cdot S_{A'B'}/(S_{A'}S_{B'}).$$

For the solubilities $S$ we can write the general Boltzmann equation

$$S = N'/N = \int dq_1 \ldots dq_n e^{\frac{Q(q_1 \ldots q_n)}{RT}},$$

and the calculation can be carried out if we can evaluate the several integrals in the expression. It is of interest, however, to note the solution which an approximate method yields. If we consider the energy change $Q$ to be independent of the co-ordinates of the phase cell and constant over the phase cell of solute molecules, then we can write, following Horiuti [24]

$$S = e^{Q/RT} \int dq_1 \ldots dq_n = \alpha e^{Q/RT}.$$

Introducing these values into the expression for $K'$, the heats of solution merely affect the activation energy, whereas the probability of the collided state (corresponding to collision number) is multiplied by the factor $\alpha_{A'B'}/\alpha_{A'}\alpha_{B'}$. If we further approximate by setting

$$\alpha_{A'} \sim \alpha_{B'} \sim \alpha_{A'B'} \sim 10^{-2}$$

(basing this value on the conclusion put forward by Horiuti [24]) the collision number in solution appears to be a hundred times higher than the collision number in the gas phase.

If we take as the normal collision number * in the gas phase

[24] Horiuti, Z. Electrochem., 1933, 39, 22.

* The most reliable way of calculating collision number seems to us to be from the molecular velocities and the mean free paths. Using this method, we arrive at the following values for widely differing gases :—
Acetone $2 \times 10^{10}$; Helium $6 \times 10^9$; Argon $6 \times 10^9$; Neon $4 \times 10^9$; Nitrous oxide $1 \times 10^{10}$; Benzene $2 \times 10^{10}$; Methyl propyl ether $2 \times 10^{10}$.

approximately $3 \times 10^9$ to $2 \times 10^{10}$, then bimolecular collision number in solution is $\sim 10^{11}$ to $10^{12}$. This is supported by the table given by Moelwyn Hughes,[25] in which a very large number of reactions have values of collision number in the region $10^{11}$ to $10^{12}$. There are many reactions which show collision numbers smaller than this, and in these cases we suggest the discrepancy might be due to the operation of a steric factor of the order of $1/10$.

It is, however, premature to draw detailed conclusions since the approximations we have made for the solubility are certainly very rough as may appear from the fact that they would yield activities always proportional to concentrations. Nevertheless, it seems worth while to compute by this method the value of the collision number between solvent and solute molecules.

Consider the components of the reaction in the gas phase

$$A' + S' \rightarrow A - S',$$
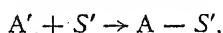
where $S'$ is the solvent molecule and $K' = KS_{A'S'}/S_{A'}S_{S'}$. If we express the vapour pressure curve for the solvent in an exponential form $S_{S'} = \beta e^{+\lambda/RT}$, where $\beta \sim 10^{-3}$ and the solubilities are expressed as before, then $K' = K\alpha_{A'S'}/\alpha_{A'}\beta$. The heat effects as before are absorbed into the activation energy term of the process, and setting $\alpha_{A'} \sim \alpha_{A'S'}$ the collision number is $1/\beta$ or $10^3$ times the value in the gas phase. If the collision number in the gas phase is $\sim 3 \times 10^9$ to $2 \times 10^{10}$, this yields a value for the collision number in solution of $\sim 10^{13}$.

Information on the collision number between solute and solvent molecules is afforded by the examples cited by Moelwyn Hughes,[26] in which the factor independent of temperature ranges mostly between $10^{12}$ and $10^{14}$. In Table I. are the observed collision numbers as recalculated from the experimental velocity constant $k$ and the Arrhenius activation energy.

| Reaction. | Solvent. | Z. |
|---|---|---|
| Malonic Acid | $H_2O$ | $10^{11}$ |
| Dimethyl Malonic Acid | $H_2O$ | $10^{13}$ |
| *Meso*-Oxalic Acid | $H_2O$ | $10^{13}$ |
| Triethyl Suphonium Bromide | $PhNO_2$ | $10^{14}$ |
| Trinitro Benzoic Acid | $H_2O$ | $10^{13}$ |
| Trinitro Benzoic Acid | $PhNO_2$ | $10^{14}$ |
| Trinitro Benzoic Acid | $PhCH_3$ | $10^{12}$ |
| Trinitro Benzoic Acid | PhCOMe | $10^{10}$ |
| Camphor Carboxylic Acid | PhCOMe | $10^{13}$ |
| Trichloracetic Acid | $PhNH_2$ | $10^{14}$ |
| Acetone Dicarboxylic Acid | $H_2O$ | $10^{14}$ |
| Allyl Malonic Acid | $H_2O$ | $10^{11}$ |
| Phenyl Benzyl Methyl Allyl Ammonium Bromide | $CHCl_3$ | $10^{16}$ |
| Triethyl Sulphonium Bromide | $C_2H_2Cl_4$ | $10^{16}$ |
| Triethyl Sulphonium Bromide | $CHCl_3$ | $10^{18}$ |
| Triethyl Sulphonium Bromide | $Pr^\alpha OH$ | $10^{16}$ |
| Triethyl Sulphonium Bromide | $CH_3COOH$ | $10^{14}$ |
| Benzene Diazonnium Chloride | $H_2O$ | $10^{12}$ |
| *m*-Toluene Diazonnium Chloride | $H_2O$ | $10^{13}$ |
| *o*-Toluene Diazonnium Chloride | $H_2O$ | $10^{13}$ |
| *p*-Toluene Diazonnium Chloride | $H_2O$ | $10^{14}$ |

[25] Moelwyn-Hughes, *Kinetics of Reaction in Solution*, page 79, Table II. (Oxford University Press, 1933).
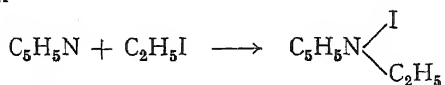[26] Moelwyn-Hughes, *ibid.*, p. 164, Table IV.

## Activation Energy at Constant Volume and Constant Pressure.

All theoretical considerations of collision numbers are only approximate so long as it is impossible to evaluate the factors entering into $K$ or $K'$ apart from the energy (see partition functions). Especial difficulty arises in solution, from the interaction between solvent and solute, which depends strongly on the temperature. This effect would be to some extent eliminated by measuring the temperature coefficients at constant volume, instead of the current method of constant pressure. The following example illustrates how strongly this correction, which would eliminate the influence of thermal expansion of the solvent, would affect the activation energies.

$$\left(\frac{\partial \log k}{\partial T}\right)_v = \left(\frac{\partial \log k}{\partial T}\right)_p + \left(\frac{\partial \log k}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p.$$

For the reaction

$$C_5H_5N + C_2H_5I \longrightarrow C_5H_5N {\overset{\displaystyle I}{\underset{\displaystyle C_2H_5}{\Big\langle}}}$$

in acetone we have from the experiments of Gibson Fawcett and Perrin,[16] at 30° C. and 1 atoms.

$$\left(\frac{\partial \log k}{\partial p}\right)_T \geqq \frac{0\cdot 9}{3000}.$$

The coefficient is calculated from the data measured at atmospheric pressure and at 3000 atms. The inequality sign is used on account of the observed decrease of the pressure coefficient with increasing pressure. For acetone we have the values

$$\left(\frac{\partial p}{\partial V}\right)_T = \frac{1}{112\cdot 0} \times 10^6,$$

$$\left(\frac{\partial V}{\partial T}\right)_p = 1\cdot 32 \times 10^{-3}.$$

So that

$$\left(\frac{\partial \log k}{\partial T}\right)_v \geqq 1\cdot 12 \left(\frac{\partial \log k}{\partial T}\right)_p,$$

hence the activation energy if the temperature coefficient is measured at constant volume is $1\cdot 12$ times larger than the ordinary activation energy, in this case the increase would be from 14,400 cals. to 16,100 cals. The true increase would probably be appreciably greater if the true value of $(\partial \log k/\partial p)_T$ were introduced.

## Conclusion.

I. The reaction velocity constant of any chemical reaction (which is not a chain reaction and in which it is not the rate of energy supply which determines the reaction velocity), can be expressed by the equation $k = \frac{1}{2}Kv$, where $K$ is the " equilibrium constant of the transition state " and $v$ is the thermal velocity of the representative point of the reacting system at the top of the energy barrier. If this equation is used in its most general sense then $K$ should stand for the probability of the transition state as some function of the instantaneous concentrations, and $k$ expresses the instantaneous reaction velocity proportional to the same function of

the concentrations. If one modifies the environment in which the reaction takes place (changing some variable $f$ by $df$), the effect on the reaction velocity will be

$$\frac{d \log k}{df} = \frac{\alpha - \alpha'}{RT} + \frac{d \log v}{df}.$$

The second term is mostly negligible, while in the first term $(\alpha - \alpha')$ has the meaning of the energy change proportional to $f$ between the initial and transition state.

Different possibilities for $f$ and $\alpha$ have been discussed, but only the case of the influence of hydrostatic pressure on reaction in solution has been worked out in detail. If $f = \pi$ (hydrostatic pressure) then $(\alpha - \alpha')$ is the volume change between a molar solution of the reactants in the initial state and the same system when all the reactants are in the transition state.

It has been shown how the influence of the environment on the rate of reaction (as in the case of a complete replacement of the solvent) might be tentatively calculated by integrating equation (i) under the assumption that $(\alpha - \alpha')$ is a constant.

II. Application of the equation $k = \frac{1}{2}Kv$ can be made by calculating $K$ by means of statistical mechanics. A few problems have been discussed from this point of view, especially the so-called " Slow reactions."

III. The equation $k = \frac{1}{2}Kv$ can be considered as a generalisation of Brønsted's equation. The generalisation implies a strict interpretation of the original Brønsted equation and also the determination in principle of the constant left undefined in it.

We have made an attempt to calculate this constant for reactions in solution which has led us to an approximate theory of the collision number obtaining between solute molecules and also between the solvent and solute molecules.

The authors wish to thank Professor E. Wigner for many helpful discussions.

# REVIEWS OF BOOKS.

**Dielektrisches Polarisation.** By O. Fuchs and K. L. Wolf. Hand und Jahrbuch der Chemischen Physik, Band 6/ Abschnitt 1B. (Leipzig : Akademisches Verlagsgesellschaft M.B.H., 1935. Pp. x + 237-460, 63 Diagrams, Indices, and separate Table of electric dipole moment measurements, pp. 36. Price 27 Rm. nett.)

The authors of this book are both well known to workers in the field of molecular structure, not only for their original work but also for their monographs. In 1932 they contributed an article on Molecular Structure and Electrical Properties to the compendium on Stereochemistry which was edited by von Freudenberg, in which they dealt with the uses of the Kerr effect and more especially of electric dipole moments in the elucidation of structural problems. Most of the present book is devoted to covering the same ground, but the treatment is more detailed, being about twice as long as the earlier article. In accordance with the wider scope which the title implies, sections on the polarisability of liquids and of solids are added.

The first part of the book, about polarisation as a physical phenomenon,

on the whole follows the lines established by Debye's book in 1928. Like the first part of that book, it is written from a pre-quantum point of view, which is adequate for most purposes and certainly is easier for most of us to understand. For those who can appreciate it there is a small section on the application of wave-mechanics to the problem and a discussion of the special results which follow from this treatment and not from the classical one. This first part is clearly written, includes considerable detail, and has adequate experimental data to illustrate various points.

In their discussion of atomic polarisation, or " infra red " polarisation, the authors describe their own procedure of allowing for it as 15 per cent. of the electron polarisation at infinite wave-length, but they do not appear to mention the fact that many workers follow Debye's suggestion of taking the molecular refractivity for the sodium D line, or the mercury green line, to give an approximate measure of the sum of the electron and atom polarisations. Nor do they make clear that, from the facts which were adduced at the Discussion on Electric Dipole Moments which was held by the Society last April (1934), it now appears that the ancient bogey of atom polarisation is less formidable than the newer one of a general solvent effect. The title of the book might be held to justify a longer section on the use of molecular refractivity in structural chemistry.

The section on experimental methods of determining dielectric constant is not very full, but this is largely compensated for by the fact that numerous references are given.

The section on the relation between dipole moment, polarisability, and molecular structure, although in some ways excellent, is in other ways rather old-fashioned. Thus, the question of the moments of bond is discussed only as a deformation of one ion by another, and not as a hybridisation of the bond between a non-polar, or weakly polar, covalent form and a polar, deformed ion-pair. Although, so far, not too much progress has been made in correlating the moments of bonds with other properties, certain attempts which have been made to correlate them with the positions of the bonded atoms in the Periodic Table deserve fuller mention. Again, in dealing with the question of valency angles, they give only the old calculations based on the idea of the deformation of one ion by others ; no mention is made of the wave-mechanical theory of directed valency introduced by Pauling and Slater. As further examples there may be mentioned the formulation of nitric óxide with a plain double bond and of the azide group with a pentacovalent nitrogen atom. In view of this it is not surprising that they miss the real point in connection with the azides, which is that the moments show that neither one of the linear structures can be correct, and that the actual structure must be a hybrid if it is linear.

The Table of electric dipole moment measurements is very useful as it stands, but it would be even more useful if an indication of the experimental method used were put alongside each number referring to a paper, rather than alongside the paper to which it refers.

Against these criticisms should be set the facts that the book contains many interesting ideas and a vast number of interesting facts, and that, except for rather an undue amount of the text being in the footnotes, it is well and clearly written.

L. E. S.

**International Conference of Physics.** London, 1934. Published by the Physical Society of London, Printed at the University Press, Cambridge. 3 vols. Pp. 257 + 183 + 40. Price 10s., 10s. and 2s. 9d. respectively, obtainable separately.

The International Conference on Physics (1934) was organised by the International Union of Pure and Applied Physics acting together with the Physical Society. This Conference is probably the largest of its kind that has been held in London and we turn with the greatest interest to the report of the proceedings. Some 200 distinguished physicists attended either as Delegates of the National Committees adhering to the Union or as guests of the Conference ; in addition the roll of members contained over 600 names. The meetings were held partly in London and partly in Cambridge. Professor Sir Frederick G. Hopkins (President of the Royal Society) gave a hearty official welcome to all members of the Congress. The report consists of three parts which we will deal with briefly in order.

## VOL. I.—Nuclear Physics.

Back in the 'nineties chemists and physicists were calmly settling down ꞏn the comfortable conviction that everything essential had been learned concerning the atom. Atoms seemed to be like ' manufactured articles' made by the multi-million, all alike except that some had more stuff in them than others. Discoveries made by Lenard suggested that there was something more to be found out but these attracted comparatively little attention. It was not until 1895 that Röntgen ' fired the shot heard round the world ' and the scientific world woke up.

In his opening survey of nuclear physics Lord Rutherford starts the story with a recognition of the extent to which our knowledge has been derived from the study of radioactive bodies and from the utilisation of the energetic $\alpha$-particles and $\gamma$-rays spontaneously emitted from elements These radioactive bodies provide a stream of swift particles—$\alpha$-particles —with which to bombard other atoms and break them up. It is a story with which no one is more familiar than Rutherford himself ; most of his own investigations have been concerned with this fundamental problem.

In the compass of eleven pages he gives a masterly and lucid outline of the main discoveries that have so far been made. It is an unfinished progress ; in fact, it is now at its height and in a most exciting stage.

The number of papers contributed left comparatively little time for discussion. The subjects dealt with were General Quantum Theory, Natural $\beta$-decay Artificial radioactivity, Disintegration and Synthesis of Nuclei and Elementary Particles, Cosmic Radiation, etc.

## VOL. II.—The Solid State of Matter.

The opening survey was made by Sir William Bragg. He emphasised the urgent need for fuller understanding of the forces that bind atoms and molecules together. In recent years new powers have been acquired of examining the structure of a solid. In consequence the growth of knowledge has been rapid. These new methods largely depend upon the use of X-rays. Diffraction gratings (*i.e.*, regular series of lines) are used to analyse light into spectra ; so (but conversely) X-rays are used

to obtain information concerning the regular structures in crystals and even in apparently amorphous bodies such as woods and vegetable fibres generally, nerve and muscle, hair and wool.  The measurements on crystals can be made with great precision ; measurements of the length of the cubic element of the rocksalt structure made by different investigators on various specimens differ by less than one part in a thousand.  " It is also gratifying to see in the details of the structures that are revealed, the origins of many of the phenomena which the crystals themselves display such as the manifold yet invariable details of form, the existence of cleavage and the position of the cleavage plane, the hardness of the diamond, the fibrous appearance of asbestos and so forth."

Yet there are phenomena of the solid state which they cannot of themselves explain.   The strength and rigidity of a crystal may vary enormously while there is no change in the X-ray indications and therefore none in the geometrical structure of the crystal.   There are properties which depend upon atomic relations which are not fully developed within the cell :  a larger field is required.   And somewhere in this scale of sizes there enters the breath of life to control those atomic compositions which enter into the living organism.

These quotations illustrate some of the properties which were enquired into in the papers contributed to the Congress by E. Hückel, F. Hund, J. M. Robertson, A. Joffé, E. Orowan, A. Smekal, W. G. Burgers, E. Schmid and others.   They are printed in full in this report together with the discussions that took place thereon.

### Vol. III.—Reports on Symbols, Units and Nomenclature.

This volume reports the decisions approved by the General Assembly of the International Union at the meeting held on the final day (5th October, 1934).  Here we breathe a very different atmosphere.  It is a very solemn matter for an International Union to express *any* opinion.  It is, of course, all done in the light of the sun—a committee of five, who have been collecting the information obtainable from many National Committees. The difficulty of securing world-wide unanimity is shown by the fact that in the final decisions alternative Symbols are published as permissible for three out of the five thermal quantities specified.  A hypercritical person might also express surprise that in a promulgation concerning units a *pressure* should stand for a generalised *force :* but we quite understand the interpretation which it is intended that we should make.  Such verbal peculiarities arise in national as well as in international legislation.

### Fine Structure in Line Spectra and Nuclear Spin.  By S. Tolansky.
(London :  Methuen & Co., Ltd.   Pp. viii + 112, with numerous diagrams.  1935.  Price 3s. net.)

This is the latest addition to the well-known series of Methuen's monographs.  Dr. Tolansky has himself made numerous contributions to our knowledge of fine structure, and is exceptionally well qualified to explain the technique, both theoretical and experimental, to research workers and others.

As a subject of study, modern spectroscopy is somewhat peculiar, and needs for success almost a special type of mind : largely the pre-requisite is a facility for dealing rapidly with the characteristic symbolism which

has been developed, and to translate its profound significance into a mental image enabling the investigator to anticipate the spectral nature of some untried atomic species. The vector methods now commonly adopted are not, as a rule, specially familiar even to advanced students, and therefore the remarkably clear treatment given by the present author is most welcome. Again, with all the will in the world, it is not easy to find help with this particular matter, and thus its inclusion in a manual such as this should be a very real boon.

Multiplicity is very fully considered (having regard to the size of the whole book), and the specific nature of LS and jj coupling comes out clearly. It is becoming more and more important to be able to think accurately in terms of both spectroscopic and magnetic evidence : Dr. Tolansky's little volume should clear the air a great deal so far at least as the former is concerned, and for the non-specialist these pages are readable and of very general interest.

F. I. G. R.

**Solid Geometry.** By L. LINES. (London : Longmans Green & Co. Pp. 292 + xx. Price 6s.)

This book is intended for Higher School certificate students. It will be of interest, however, to others who, having forgotten most of what they knew of solid geometry, wish to follow modern work on crystal structure. The subject is well and clearly set out.

**Exploring the Upper Atmosphere.** By DOROTHY FISK. (London : Faber & Faber. Pp. 166. Price 6s. net.)

The objects and methods of investigation in the troposphere and lower stratosphere are discussed in simple language. The book is very readable. There is a short introduction by Professor H. L. Brose.

**Alternating Currents.** By ALBERT E. CLAYTON. (London : Longmans Green & Co. Pp. 334. Price 10s. 6d.) Second Edition.

Eleven years have passed since the issue of the first edition. The scope has now been extended so as to cover the work students are likely to need in their third as well as in their second years.

**The Laboratory : Its Place in the Modern World.** By Dr. STARK MURRAY. (London : The Finland Press. Pp. 117. Price, 2s. in paper, 3s. in cloth.)

This book by a pathologist presents research to the lay reader. Naturally there is a medical bias.

**A Symposium on Illumination.** (London : Chapman & Hall. Pp. xv + 229. Price 13s. 6d.)

Here are collected the lectures delivered under the auspices of the National Illuminating Committee of Great Britain and the Illuminating Engineering Society in the spring of 1933. The lectures are of considerable interest, each dealing historically with a particular feature, and it was worth while to preserve them in this permanent form.